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MEMOIRS OF THE GEOLOGICAL SURVEY.

SPECIAL REPORTS ON THE MINERAL RESOURCES OF GREAT BRITAIN.

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VOL. XVI. — REFRACTORY MATERIALS: GANISTER AND SILICA-ROCK — SAND FOR OPEN-HEARTH STEEL FURNACES — DOLOMITE.

PETROGRAPHY AND CHEMISTRY.

BY

HERBERT H. THOMAS, M.A., Sc.D.,

A. F. HALLIMOND, M.A.,

AND

ERNEST G. RADLEY.

GEOLOGICAL SURVEY OFFICE
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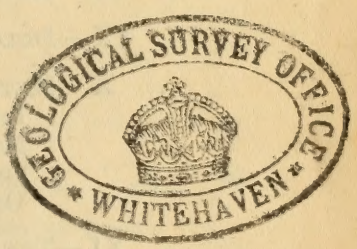

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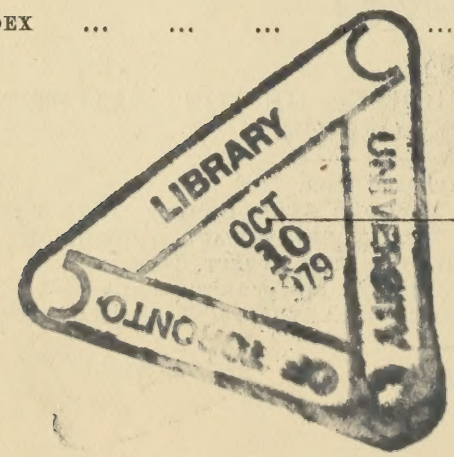

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PREFACE.

The Memoir in which the resources and geology of certain raw refractory materials were described was published in 1918 as Volume VI of the Special Reports on the Mineral Resources of Great Britain.

At that time the laboratory-work on the specimens collected, on finished products and on bricks that had been used in furnaces, was in hand, but it was not desirable to delay publication of an account of the field-work for an investigation which was likely to occupy some months. The call for a Second Edition of Vol. VI now affords an opportunity of publishing an account of the petrography and chemistry as nearly simultaneously as possible with that of the resources and geology.

An investigation of the materials used for silica-bricks and for hearths in furnaces calls especially for petrographical methods as supplementary to chemical analysis. The questions that arise are intimately connected with the theory of crystal-growth and chemical equilibria, under conditions that are analogous to those which obtain in the formation of igneous and metamorphic rocks.

The present work deals more especially with the application of these principles to the manufacture and use of silica-bricks. An account is given of the petrographical characters and chemical composition of the raw material and of the manufactured brick before and after its use in the furnace. Special attention is paid to the allotropic modifications of silica and to the degree of conversion produced in the quartz of the original material.

The literature dealing with the silica-refractories is large and scattered, and while due consideration has been paid to all new observations and well-established facts, it has been thought undesirable to burden the text with copious references which have for the most part been given elsewhere.

The basic process is of ever increasing importance and its use has been widely extended during the past five years. In the concluding chapters of the present Memoir will be found an account of the petrographical characters and chemical composition of the dolomites, the methods of analysis of dolomites and dolomitic rocks, and of the changes produced in hearths made of these materials. Little published information exists on this subject, particularly on the changes that take place in the basic hearth during service, and in this direction an interesting field of research lies open.

Thanks are due to Mr. Arthur Acton who has furnished valuable information and advice on the raw material and process of manufacture, and to Dr. Pollard, late Chemist to the Geological Survey, who has kindly read Chapter X. towards which he has contributed valuable suggestions. Thanks should also be accorded to a number of private individuals and firms who have rendered assistance to our officers in the field and who have been so ready to supply information and material for the purposes of this Memoir. Special thanks are due to the South Durham Steel and Iron Co. (Malleable Works) who through their chief chemist, Mr. J. H. Whiteley, have furnished material of the greatest assistance in the preparation of those portions of the Memoir dealing with the furnace-structure, and also to Dr. J. E. Stead, F.R.S., for permission to publish his analyses of a brick that has been used in the roof of a steel-furnace, and for the loan of micro-sections.

A. STRAHAN,
Director.

Geological Survey Office,
28, Jermyn Street,
London, S.W. 1,
27th November, 1919.

REFRACTORY MATERIALS.

SILICA ROCK, SAND AND DOLOMITE.

PETROGRAPHY AND CHEMISTRY.

CHAPTER I.

Silica-Rocks.

Introduction.

The silica-rocks used for the manufacture of silica-bricks belong to two main groups, quartzites and sandstones. These groups have no well-defined limits of texture or composition and in certain cases merge into one another, and include the subordinate group of rocks known as ganisters.

In this volume it is proposed to treat these silica-rocks from the point of view of their texture, composition, and suitability for the manufacture of refractory bricks, irrespective of their geological age and distribution which have been fully dealt with in Vol. VI. of the 'Special Reports.'

Detailed descriptions of many of the rocks used in the making of silica-bricks have also been given in the earlier volume, but it has been thought desirable to present a more general and collective account of the various rock-types now in use, and to set out their chief features as a guide to the future exploitation of the raw material.

There still exists considerable confusion in the nomenclature of the silica-rocks, due in some cases to the too literal interpretation of geological terms, and in others to the use of geological terms for trade-purposes irrespective of their scientific meaning. For instance, the name *ganister* has been extended so as to embrace a whole series of rocks which are quite distinct from those originally described under this name and of which many would, scientifically speaking, find a more justifiable position under the heading of some other group.

It is impossible, however, at this stage, if we retain the terms in general use, to correct the errors that have been introduced, but we have set out below, in some detail, what may be regarded as the essential characteristics of the groups in question and have entered into some discussion as to how far a wider application of the respective group-names is justified.

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Sandstones.

A sandstone is a detrital, arenaceous deposit, of which the component grains have been furnished by rocks disintegrated by natural agencies. The grains may vary greatly in size and shape and be of any material, but quartz is usually the dominant constituent. Micas, chlorites, felspars, and other minerals, fragments of calcareous organisms and calcareous or siliceous sediments, may also enter largely into their composition. Generally the grains are rounded, but in some cases angularity of grain is a distinctive feature. As a general rule, the angularity varies inversely with the size of the particles.

The term *grit* has often been used synonymously with sandstone, but strictly speaking it should be employed as a varietal designation of those sandstones of which angularity of grain is a conspicuous feature.

The grains of a sandstone are naturally restricted to those minerals that could best survive rolling and weathering, and belong more particularly to those mineral species that could be furnished by the larger masses of igneous and metamorphic rocks such as those of granites, gneisses and schists.

It follows, therefore, that the hard or stable minerals such as quartz, muscovite, and some of the felspars are more likely to be the dominant minerals present, and that such easily decomposed minerals as the ferro-magnesian silicates olivine, pyroxenes, hornblendes, biotite, etc., will be of much less frequent occurrence.

The *cementing material* may be siliceous, calcareous or ferruginous, but occasionally such minerals as barytes or gypsum may act as cements.

In addition to the actual cement there exists what may be termed *interstitial matter*, that is to say fine granular detrital material that acts as packing to the larger grains. With spherical grains this interstitial matter may reach a maximum, but with an increase in angularity and the consequent closer packing of the larger grains the space for it tends to diminish.

In practice the various kinds of sandstones are distinguished by reference to their mineral-composition and to their cementing-material. Terms such as *quartzose*, *micaceous*, *felspathic*, etc., referring to definite minerals, are used to designate important or characteristic mineral-grains present in the rock, but such general terms as *calcareous*, *siliceous*, *ferruginous*, etc., in which no mineral is particularised, are employed to indicate the nature of the cementing material. Thus, *quartzose ferruginous sandstone* will convey the idea of a rock composed largely of quartz-grains with compounds of iron acting as the cementing-matter.

Sandstones are, for the most part, somewhat soft rocks, their friability being determined by the shape of the constituent grains, by the nature of the cement and by the extent to which cementation has taken place.

They have generally a rough, uneven fracture, giving rise to dull surfaces except in those cases in which the original quartz-grains have been given bright crystal-faces by the addition of secondary silica.

Almost all sandstones are porous to some extent, the porosity being due to an incomplete filling of interstitial spaces by cementing-material, and such sandstones are therefore liable to become stained by the introduction of mineral-matter in solution, and to suffer loss of cohesion by the extraction of some of their soluble constituents.

Being sedimentary rocks, sandstones usually show bedding-planes that mark pauses in their deposition.

Joints caused by contraction during consolidation subsequent to deposition usually traverse the rock at right angles to the bedding-planes, and these joints, together with the bedding-planes, often determine the workability or otherwise of any particular stratum.

Quartzites.

Quartzites are highly siliceous rocks which consist essentially of interlocking grains of quartz with a siliceous cement in those cases where interstitial spaces allow of the presence of cementing-material. They may originate from quartzose sandstones in two distinct ways, either (1) by silicification due to the introduction of soluble silica or (2) by complete thermal alteration resulting in a recrystallisation of the quartz and the obliteration of the original clastic structure.

Quartzite, formed by the introduction of soluble silica into a quartzose sandstone, may be said to represent the more completely cemented variety of quartzose siliceous sandstone. The introduced silica has filled all the interstitial spaces, and has grown in crystallographic continuity with the grains that it binds together. The initial stages of such a silicification are often made noticeable in the siliceous sandstones by the addition of quartz in such a manner as to give well-defined crystal-outlines to the original irregular or rounded grains of this mineral. A well-known example is the partly silicified sandstone of Penrith.

The production of a quartzite by the thermal metamorphism of a pure quartzose sandstone is the only change met with in such a rock when subjected to the high temperature of invading igneous masses. The change is brought about by the destruction of the original quartz grains and their recrystallisation as a mosaic of interlocking and mutually interfering quartz-crystals.

Certain other constituents of the original rock, such as white mica and detrital zircon, garnet, etc., may escape alteration, and these may give some indication as to the original stratification of the metamorphosed rock. Whatever be their origin, quartzites have many points in common, for, apart from their highly siliceous composition, they have similar degrees of hardness, and fracture gives rise to smooth sub-conchoidal surfaces.

The more chemically pure quartzites are white, but staining is a common feature, and may be either original or subsequently introduced. The most common colouring matter is hydrated oxide of iron, imparting a yellow or reddish brown colour, and less often the anhydrous oxide, hæmatite, which gives the deep red colour to ferruginous quartzites that approach jaspers in composition. Occasionally these rocks, more especially those

which occur in the Carboniferous System, assume a grey colour, due to the presence of finely-divided carbon as interstitial matter. With increasing impurity, the presence of minerals other than quartz, such as chlorite, glauconite, etc., may impart characteristic colours to the rocks.

Ganisters.

The term 'ganister' had originally a perfectly definite geological significance, and was given a place in their nomenclature by the early geologists. It was applied with absolute precision to siliceous rocks that occur in the Lower Coal Measures of the Sheffield district, and possess definite physical characters. The original definition was determined not only by the character of the rock but by its geological age and by the locality in which it occurs. The definition of a rock-type should be independent of considerations of geological age and locality, and therefore the extension of the original term 'ganister' to include identical rocks occurring elsewhere and in other geological formations would be legitimate, provided that the rock be defined by strict reference to its physical characters and chemical composition. Unfortunately, the name has been applied as a trade-name to rocks which show a marked divergence from the type, thereby reducing its significance and value. Strictly speaking, there is no scientific need for the retention of the term 'ganister,' for such rocks may be adequately described as variants of sandstones or quartzites, but its firm establishment as a trade-name favours its retention, provided it be used in a conscientious manner to denote rocks with certain definite physical and chemical properties.

The true ganisters of the Sheffield district are fine-grained bedded siliceous rocks, composed of angular quartz-grains closely packed and cemented by secondary silica. The grains, owing to their angularity, fit closely together and thus the interstitial spaces are reduced to a minimum. Further, the grains are remarkable for the uniformity of their dimensions, which range from 0·05 mm. to 0·15 mm. These rocks are typically composed of quartz; other minerals usually present in arenaceous rocks, such as mica, felspar, etc., are rare. In the cementing material, carbonates and iron compounds play quite a subordinate part. Only a small quantity of interstitial matter is present, and this contains a fair proportion of finely-divided carbonaceous matter that gives to these rocks their characteristic pale to dark grey colour. Dark streaks and patches are of common occurrence and these are, in general, carbonaceous remains of plant-stems and rootlets, and are similar to those ordinarily met with in fire-clays.

The ganisters break with a splintery to sub-conchoidal fracture, giving rise to fragments with sharp edges, and finely-granular surfaces. They are usually jointed in a rough manner and break more readily along the joints than along the bedding-planes, which are often quite indistinct. Staining of these rocks, usually of a ferruginous nature, has taken place in many cases along the joints, and to a less degree along the bedding-planes, but the

general impervious character of the rocks in question seldom allows the staining to be more than superficial.

The Sheffield rocks must be adopted as the type with which all other rocks of similar character should be compared, as they originally bore the name of 'ganister,' were some of the earliest worked silica-rocks for the purpose of the manufacture of silica-brick, and are undoubtedly of the highest purity. (*See* Chap. III., p. 16.)

With regard to the latitude that may be given to the usage of the term 'ganister,' it may be pointed out that a slight increase in the quantity of constituents other than quartz, slight variations in the size and angularity of the component grains, and slight differences in the nature of the cementing materials, such as the introduction of a small proportion of calcium carbonate, may be allowed. Thus certain rocks of the Carboniferous System in the South of Scotland, which differ in the above respects from those of Yorkshire, and a limited number from other areas, would be included, but many silica-rocks, at present known as 'ganisters,' must be excluded. These variations will be dealt with more particularly in Chapters II and III, in which the petrographical characters and chemical composition of the various rocks will be discussed in detail.

CHAPTER II.

Petrography of the Silica-Rocks.

Introduction.

The rocks that are, and have been, used for the manufacture of silica-bricks, although they have the common characteristic of a high silica-percentage, present variations which affect the treatment to be accorded to them, and the character of the manufactured article. These variations may be grouped under the following headings:—

1. The microscopic structure.
2. The mineralogical composition.
3. The nature and amount of the cementing material.
4. Naturally-introduced impurities.

The textural characters of a silica-rock have perhaps the most important bearing on its suitability for the manufacture of silica-bricks. A careful comparison of the size, shape, and closeness of the component grains is therefore likely to yield valuable information.

With regard to mineral composition the chief variations take place in the proportion of felspar, mica, felspathic rock-fragments and detrital iron ore and other less common minerals which may be present, and which not only produce a reduction in the total percentage of silica, but are prejudicial by virtue of their lower melting points and chemical instability.

The cementing material varies most, for, although it is always in relatively small amount, in it are collected almost all those chemical compounds other than free silica which appear in the analyses. It is undoubtedly this material that, under the influence of firing, determines the changes that are necessary for the formation of a silica-brick. On the other hand, an undue proportion of cementing and interstitial matter, other than silica, will have a tendency to produce instability in a brick on account of the ease with which it will give rise to a superabundance of siliceous compounds with low melting-points.

Impurity introduced into silica-rocks from outside sources is usually restricted to the surfaces of joints and other planes of weakness, but in the more porous rocks it may penetrate the mass for some distance; further, it is usually more abundant in those portions of the rock which occur near the surface, and which have thus come more within the influence of oxygenated or carbonated waters carrying ferruginous, calcareous or other compounds in solution.

The Microscopic Structure.

When studied by means of thin sections the mutual relations, size and shape of the component particles, and thus the texture of a rock, can be gauged to the best advantage, and a clear idea can be formed as to the nature and amount of material other than quartz which may be present.

Ganisters and Quartzites.—The microscopic structure of the true ganisters (Sheffield type) presents certain peculiarities that entitle these rocks to special description.

The ganister that forms the floor of the Halifax Hard Mine Coal in the Sheffield District, and which is regarded as the best ganister in Yorkshire, may be taken as the type. Most of the true ganisters, such as those of Beely Wood, Wadsley, and Wood End Mine, belong to this type, but similar characters are displayed by rocks from other districts, such as those of Byerley House, Wolsingham, and Weardale in Durham, and to a less extent by those from Derbyshire and North and South Wales.

As has been stated on p. 4, the outstanding textural features are the angularity of the component quartz-grains, their general similarity of dimensions, and closeness with which they are packed together, leaving a relatively small interstitial space into which other substances can segregate.

The difference of texture presented by the other rocks employed are considerable, and depend almost entirely upon the size and shape of the grains of which the rock is mainly composed and upon the amount of interstitial matter. Generally speaking, the rocks most commonly used are characterised by the angularity and consequent close-packing of the grains, but when both grains and matrix are siliceous the close-packing is not so essential. Thus, in certain useful quartzites and other well-silicified sandstones the quartz-grains are often sub-rounded or even rounded in form. It may be set forward as a general statement, however, that rocks with rounded grains are, in the majority of cases, less purely siliceous, often less compact and more friable, that is to say less completely cemented, and more liable to have received infiltrated impurities from outside sources.

The angularity of the grains of sedimentary rocks is usually in inverse ratio to the size of the particles, a finer texture being characterised by more angular grains. In the majority of usable silica-rocks the component grains are remarkably constant in size and differ from rock to rock through such a small interval as from 0·1 to 0·3 mm. in greatest dimensions. Some rocks of variable grain, or of coarser though uniform grain, are used, but it is probable that even-grading of the component particles, and grain-dimensions of from 0·1 to 0·3 mm. are in themselves desirable characters for a silica-rock to possess when used for the manufacture of silica-bricks.

In the larger class of quartzites, excluding ganisters, we find a much greater variability of texture. The size of the component grains is no longer uniform and the angularity of grain becomes less marked. The interstitial matter is less evenly distributed, and excessive or deficient in amount. In the latter and most usual case the quartz-grains are joined together by secondary

quartz, free from impurity, in such a manner as to constitute what for practical purposes may be regarded as homogeneous quartz.

The chief quartzites used are those of Holyhead in Anglesey, the more silicified portions of the Millstone Grit of South and North Wales, and of the Millstone Grit and Oolitic rocks of Yorkshire and Durham. Well-known localities are Bwlchgwyn, near Minera in North Wales; Llandybie, Mynydd-y-gareg, the Black Mountains, Kidwelly and Garn-bica in Carmarthenshire; Penwyllt and Hirwaun in Brecon; Cleveland, Beely Wood, Hawksworth, and Wensley in Yorkshire; and Frosterley, Weardale and Knitsley Fell in Durham. In Scotland certain ancient quartzites like those of Islay, Jura and Loch Leven are quarried to a limited extent.

Quartzites may be composed of closely interlocking grains with a relatively small proportion of cementing material or of more widely-spaced grains which have been enlarged by the addition of secondary silica until all the intervening spaces have been filled with this material. Viewed from an economic standpoint the two types mentioned above differ but little.

The illustrations given on Plate II will serve to show the textural characters of quartzites, and indicate how they differ from the fine-grained and evenly-graded ganisters. (Plate I, figs. 1, 2, 3.)

Occasionally, quartzites, especially those which belong to the older geological formations, show the effect of earth-pressure in a sheared structure, and in the breaking-up and elongation of the quartz-grains in the direction of the shearing (Plate II, fig. 5.). Such changes affect the homogeneity of a rock, and may be accompanied by films of newly-developed mineral matter, beneficial or otherwise. Holyhead and the older Scottish quartzites are examples. A pure quartzite, such as that figured on Plate II, fig. 6, on crushing gives rise to particles that will behave as homogeneous quartz-grains, but rocks such as the Holyhead quartzite, and many of the less completely silicified quartzites of the Carboniferous System, have textures in common with the ganisters.

Sandstones.—The sandstones vary between much wider limits than do the quartzites and ganisters. They are generally porous to some extent and may be friable or even incoherent. Texturally they exhibit all stages from a collection of closely-packed, even-graded, angular grains to rocks composed of well-rounded fragments. Sandstones, although mainly consisting of quartz, vary in composition through the incorporation of felspar, mica, chlorite, and other detrital minerals, as well as rock-fragments, but it is in the constitution of the interstitial and cementing material that the greatest differences are observable.

Those composed almost entirely of quartz-grains, with a small amount only of interstitial matter, pass gradually, according to the amount of secondary silicification that they have undergone, into the quartzites. A good example of practically complete secondary silicification is illustrated by Plate I., fig. 5, in which angular grains of quartz, somewhat widely spaced and

of which the original outlines can be clearly seen, have been joined together to form a coherent mass by secondary silica deposited from solution. This infiltration of silica is frequently accompanied by a similar migration of titanium, bringing about the crystallization of titanium oxide as secondary brookite. Secondary brookite may be said to be an almost constant associate of secondary silica in the silicified sandstones of the Millstone Grit of Durham and Yorkshire. The amount of titanium carried by the siliceous solutions is, of course, extremely small when compared with the silica, and thus the crystals of brookite are minute and widely separated. A good example is shown in Plate I, fig. 6. Another illustration of a silicified rock of somewhat different character is furnished by Plate I, fig. 4. In this case the silicification is less complete, and the amount of interstitial impurity proportionately greater; at the same time there is greater variation in the dimensions as well as in the degree of rounding of the individual grains. Some less coherent sandstones, in which the interstitial matter bulks more largely and in which silicification has not reached such a high degree, are illustrated on Plate III. Fig. 1, from a photograph by transmitted ordinary light, shows a sandstone composed of somewhat angular quartz-grains set in a partially silicified matrix of smaller fragments. The interstitial matter, other than quartz, shows itself as turbid streaks and patches, but is not considerable in amount. Fig. 2, the same area photographed between crossed nicols, brings out the microscopic structure and more clearly emphasises the angularity of the component grains. With the increase of interstitial matter and impurity the demarcation of the grains becomes a more pronounced feature, and is frequently accompanied by the appearance of large flakes of mica and of other minerals having dimensions comparable with those of the quartz-grains.

Figs. 3 and 4 of Plate III. illustrate two impure fine-grained sandstones in which the interstitial matter and impurity reaches an undesirable amount. Moreover, this impurity is accompanied by quite a considerable quantity of mica which shows itself as narrow flakes between the quartz-grains. The variability of composition due to interstitial matter and cementing material is also well illustrated by these same figures, for they show how much greater is the bulk of that material. The opacity of the interstitial matter is in the main due to ferruginous impurity that occurs partly as granular constituents or partly as a homogeneous cement.

Analyses, however, often indicate that a rock is relatively impure while the microscope reveals little interstitial matter other than quartz. The impurity in such a case is in the substance of the component grains themselves, and such a rock is strikingly illustrated by Plate III, fig. 6. In this case the individual grains fit closely together, leaving little room for interstitial impurity, but themselves consist largely of material other than quartz, such as decomposed felspar and felsitic rock-fragments which contrast in their turbidity with the clear quartz of the rest of the rock.

The variation in the mineralogical composition of the mineral grains is easily detected under the microscope, and upon a correct identification of the minerals depends a correct interpretation of the chemical analysis. It will be obvious, for instance, that a rock that contains all its potash in the form of large grains of orthoclase felspar will have a different quality to a rock in which the potash is contained by finely-divided muscovite existing as interstitial material.

The mineral-grains usually met with are of the potash and soda-lime felspars, white mica, chlorite and iron ore—most commonly ilmenite and magnetite. Less abundant, and of smaller dimensions, are the heavy detrital minerals of sedimentary rocks such as zircon, tourmaline, rutile, etc. These, on account of their relatively small size, are usually located in the interstitial matter and seldom affect either the chemical composition or the refractory character of the rock. As we have seen, rock-fragments of a size commensurate with that of the quartz-grains may, and often do, occur in considerable quantity in the less pure siliceous rocks, more especially in the sandstones. They consist mainly of carbonaceous shale, chert, quartzite, and fine-grained siliceous and felspathic igneous rocks such as rhyolites, felsites, etc. In some instances such fragments constitute a large portion of the rock and thus greatly reduce the total percentage of silica. Such a reduction is noticeable in many of the felspathic quartzites and felspathic or micaceous sandstones. It is probable, however, that an excess of impurities in the form of large grains is not so harmful to the rock as an equal amount finely disseminated in the interstitial matter. The interstitial matter of the silica-rocks may consist entirely of comminuted fragments of the same material as that which forms the larger grains, and in this case will differ but little from it in either mineralogical or chemical composition. On the other hand it may consist in part only of such material and have incorporated a relatively large proportion of argillaceous matter such as finely-divided mica, kaolinite, and other hydrated silicates. In the quartzites (including ganisters), and in the more highly silicified sandstones this argillaceous matter is of small amount, seldom resolvable by the microscope into its component minerals, and generally only discernible as an indefinite film coating the closely-interlocking quartz-grains.

In the sandstones, however, the amount of argillaceous matter is much greater, and this increase is indicated in the chemical analyses by relatively higher percentages of alumina, potash, and water (above 105° C.). Microscopically, finely-divided muscovite is easily detected in the interstitial matter of the less pure sandstones, and kaolinite may be proved in many instances by appropriate optical tests on the powdered rock. Owing to the increased porosity of rocks with much interstitial matter there has often been an introduction of a considerable amount of iron which has stained the argillaceous material and to a great extent masked its true nature.

We have seen that in the purer silica-rocks the cementing material is entirely siliceous and is generally in the form of

quartz, and that this secondary silica has more or less firmly united the quartz-grains and has further involved any small amount of interstitial detrital matter that might have been present. In the less completely silicified rocks, although silica is still dominant, we may have other compounds playing the role of cement, such as the hydrated oxides of iron, calcite, dolomite, chalybite, and probably hydrated silicates. None of these cements has the tenacity of silica, and, therefore, the rocks in which such compounds exist in quantity are less compact than those more purely siliceous, but are, at the same time, much less friable than many sandstones which have merely a small amount of argillaceous matter, and no real cementing material, between the grains.

Next to silica, and in frequent association with it, the iron oxides exist most commonly as cementing media. Calcite and dolomite are common in small quantities, especially in the Scottish 'ganisters,' but chalybite is of exceptional occurrence. Barytes, which occasionally acts as a cement in the case of certain sandstones, has not been met with in any of the usable silica-rocks.

Passing to the subject of naturally introduced impurity, we are mainly concerned with compounds of iron and the carbonates of lime and magnesia. In the non-porous ganisters and quartzites, solutions carrying iron salts or carbonates can only penetrate the rock by means of joints and cracks, and the deposition of oxides of iron or calcite is thus confined to the faces of these fissures. It is seldom, therefore, unless the rock is extremely jointed and fissured, that the impurity introduced in this manner is detrimental in amount. A false idea of the amount of iron present in these rocks may, however, easily be gained from the fact that often almost every surface of the quarried rock is a joint-face. These are deeply stained, and practically all the iron oxide in the block is forced upon our notice. Many rocks that are conspicuously stained on joint-surfaces in this manner prove to contain a much lower total of iron compounds than many of the more porous rocks that have, superficially, a less ferruginous aspect.

It is in the sandstones that the introduced impurities bulk most largely, as is demonstrated by the microscope and is indicated by the generally higher percentages of ferric oxide and carbon dioxide. In the sandstones, however, owing to their more porous character, it is difficult to draw a distinction between cementing material and introduced impurity, for iron compounds as well as carbonates, introduced from outside sources, quite often play the part of cements to what would otherwise be more or less incoherent rocks.

EXPLANATION OF PLATE I.

FIG. 1.—"Main Ganister," West Butsfield Quarry, Durham. (Carboniferous.) Shows closely packed angular quartz-grains, about 0·1 mm. in size. The amount of interstitial matter other than silica is small. E. 11594. × 30 diams. Crossed nicols.

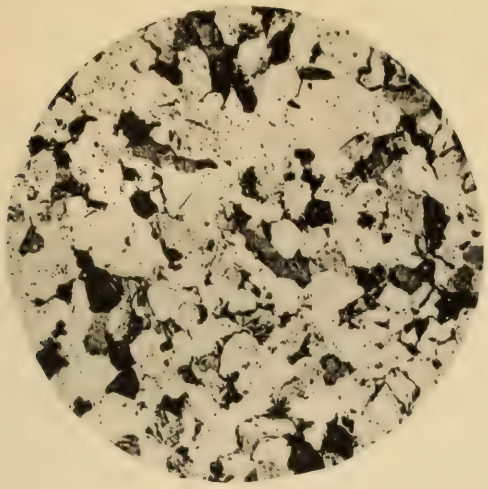
FIG. 2.—"Ganister" Knitsley Fell, Wolsingham, Durham. (Carboniferous.) Fine-grained siliceous Sandstone, slightly micaceous. Grain angular, closely packed, and averaging 0·075 mm. E. 11506. × 30 diams. Crossed nicols.

FIG. 3.—Ganister-like Sandstone, Lealholm Moor, Cleveland, Yorkshire. (Inferior Oolite.) Composed entirely of angular and sub-angular quartz-grains, mostly less than 0·1 mm., cemented by secondary silica. E. 11489. × 30 diams. Crossed nicols.

FIG. 4.—Sandstone. Castlecary Pit, Castlecary, Stirlingshire. (Millstone Grit.) The photomicrograph shows somewhat large quartz-grains, widely spaced and separated by a relatively large amount of argillaceous matter that acts as a weak bond. S. 19555. × 30 diams. Ordinary light.

FIG. 5.—"Main Ganister," Byerly House Quarry, Rowley, Durham (Lower Coal Measures). The rock is a fine-grained quartzite composed of angular quartz-grains (0·1 mm.), widely spaced and cemented by a somewhat large amount of secondary silica. It furnishes an excellent example of siliceous infilling and cementation. E. 11580. × 30 diams. Ordinary light.

FIG. 6.—Crystals of secondary Brookite, with secondary silica, in the interstitial matter of a ganister-like sandstone from Cross Quarry, Crawleyside, Stanhope, Durham. E. 11529. × 260 diams. Ordinary light.



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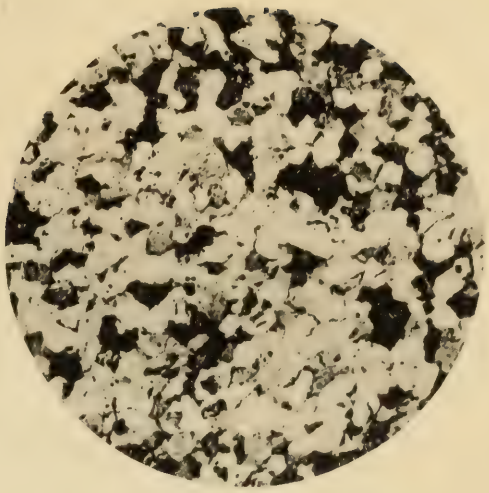

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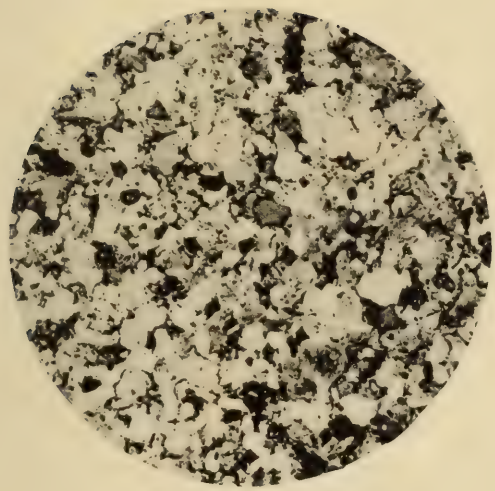

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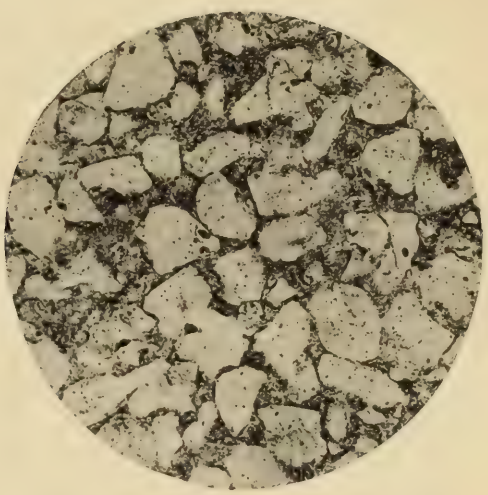

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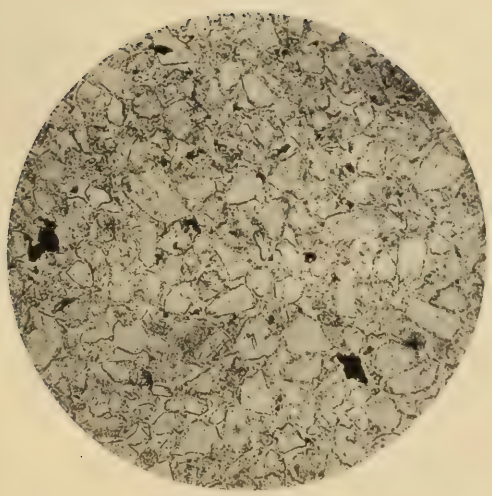

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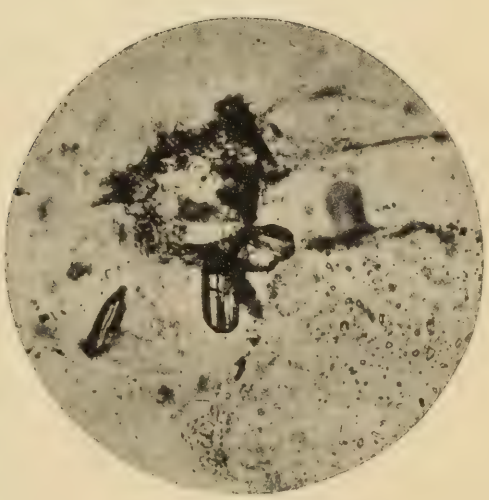

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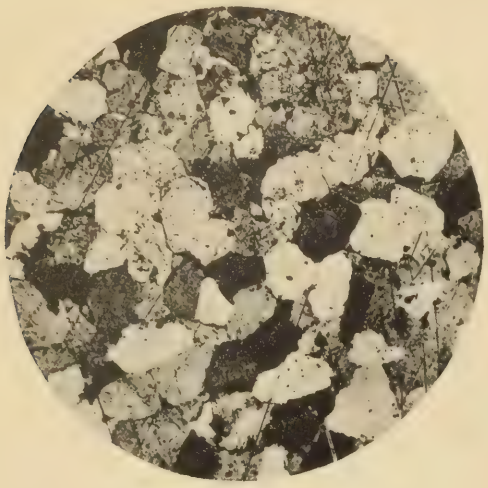

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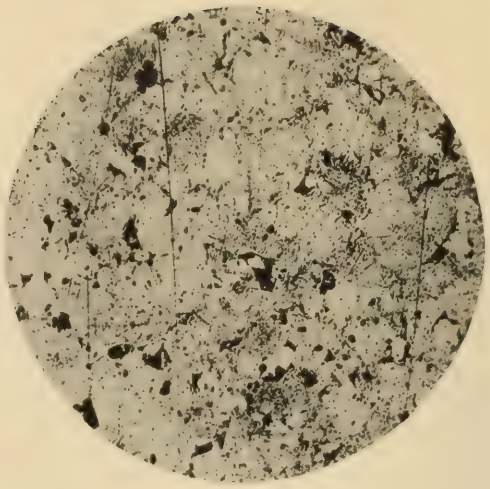

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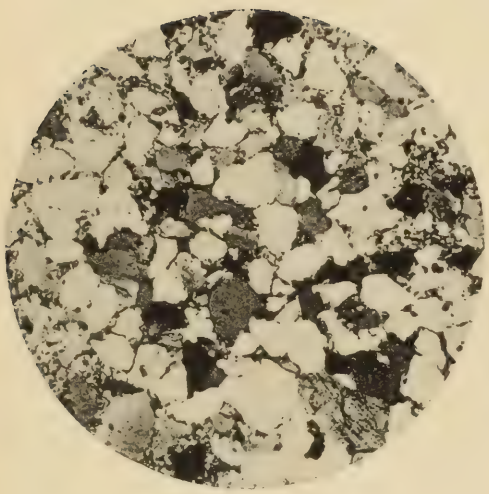

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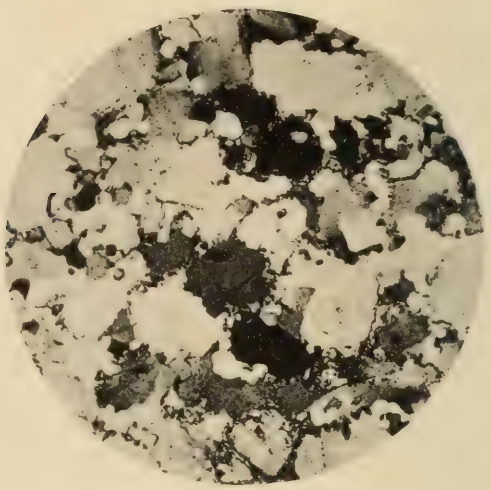

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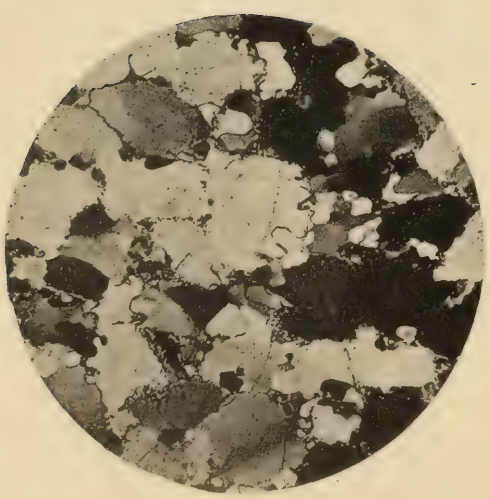

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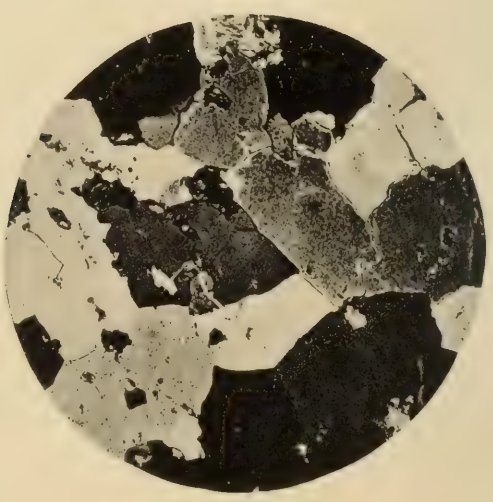

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EXPLANATION OF PLATE II.

Fig. 1.—Quartzite, Hawksworth Quarry, Windy Ridge, Yorkshire. (Carboniferous.) First-quality stone. Non-felspathic and with only an occasional flake of mica. Cement siliceous but somewhat turbid. E. 11511. × 30 diams. Crossed nicols.

Fig. 2.—Same rock as Fig. 1 photographed with ordinary light. The illustration brings out well the turbidity of the siliceous cement and interstitial impurity. × 30 diams.

Fig. 3.—Quartzose Sandstone or Quartzite. Castleton Quarries, North Cleveland, Yorkshire. (Inferior Oolite.) Sub-angular grains of quartz, about 0·15 mm., in a plentiful cement of micro-crystalline silica. "Castleton Ganister." E. 11491. × 30 diams. Crossed nicols.

Fig. 4.—Fine-grained saccharoidal Quartzite from N. of Inver Cottage, Jura, Scotland. S. 19546. × 30 diams. Crossed nicols.

Fig. 5.—Quartzite. Bonahaven Distillery, Islay, Scotland. The rock is fine-grained and completely silicified, the original quartz-grains showing fringes of micro-crystalline quartz. Shearing has produced a rough parallelism of the quartz-grains. S. 19545. × 30 diams. Crossed nicols.

Fig. 6.—Quartzite. Laganha Quarry, Duror, Argyllshire, Scotland. A coarse-grained rock composed of closely interlocking grains of quartz and perthitic alkaline felspar. Practically free from impurities. S. 19548. × 17 diams. Crossed nicols.

EXPLANATION OF PLATE III.

FIG. 1.—Sandstone. Fine-grained. Buckley, Flintshire (Coal Measures). Shows unequal grading and a moderate amount of lightly stained interstitial matter. E. 11596. × 30 diams. Ordinary light.

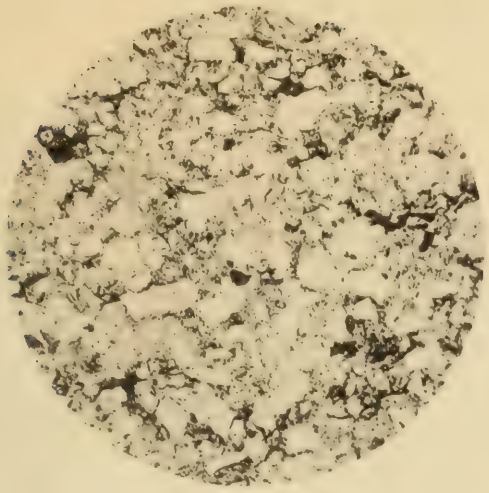
FIG. 2.—Same area as Fig. 1 seen between crossed nicols.

FIG. 3.—Sandstone. Fine-grained, impure and highly micaceous. (Millstone Grit.) The cementing matter is argillaceous and locally stained with iron. S. 19581. × 30 diams. Ordinary light.

FIG. 4.—Sandstone. Rishton, Blackburn, Lancashire. (Coal Measures.) The rock is fine-grained and composed of extremely angular quartz-grains with some mica set in a muddy matrix of finely divided quartz, iron oxide and mica. E. 11582. × 30 diams. Ordinary light.

FIG. 5.—Sandstone. Marsden Moor, Yorkshire. (Millstone Grit.) Coarse and of moderately even texture. Amount of interstitial matter small. E. 11523. × 30 diams. Crossed nicols.

FIG. 6.—Sandstone. Hermand Quarry, West Calder, Edinburghshire. (Calciferous Sandstone Series.) The rock is impure and contains much decomposing felspar. An example of a rock in which the impurities are in the substance of the grains rather than in the interstitial matter. S. 19557. × 30 diams. Ordinary light.



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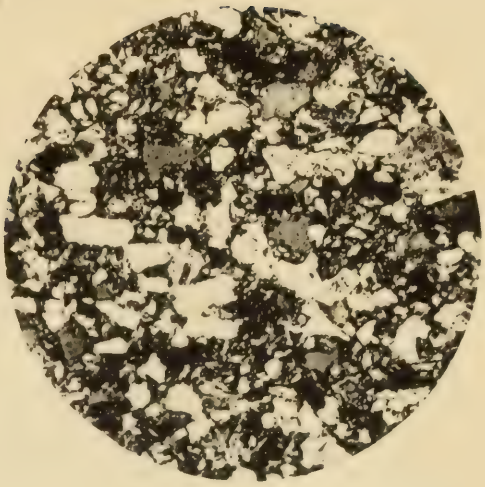

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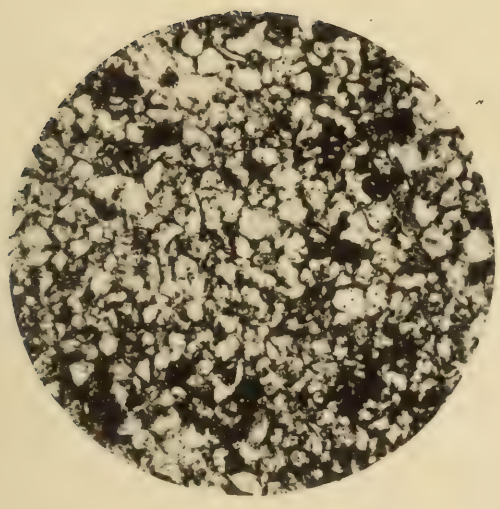

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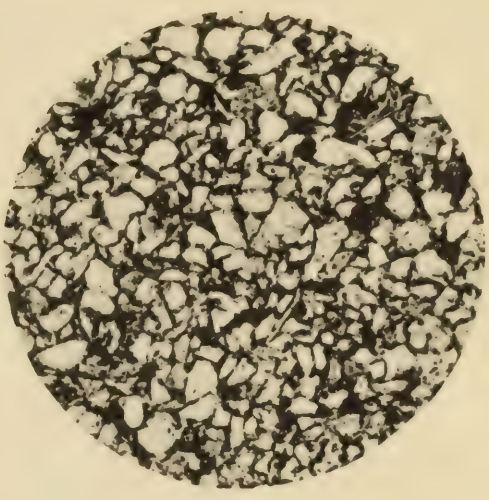

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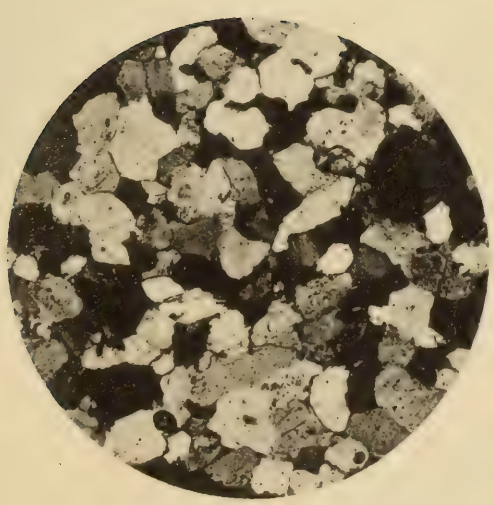

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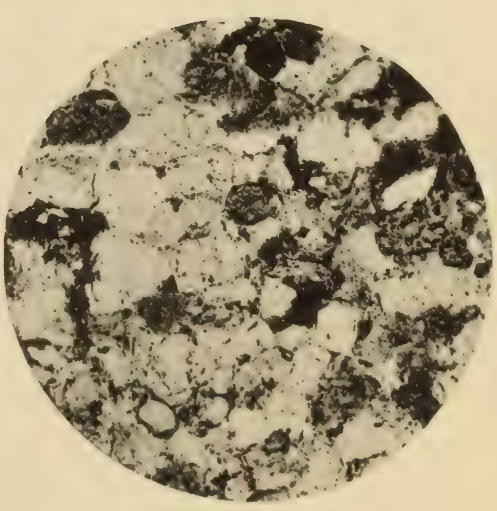

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CHAPTER III.

The Chemical Composition of the Silica-Rocks.

In the following pages we have set out those chemical analyses of typical silica-rocks which have been made in the Survey Laboratory, and have collected a considerable number of analyses from trade sources.

In view of the importance of some of the substances other than silica which occur in a silica-rock it is obvious that, small though their proportions are, too great care cannot be expended upon their correct estimation, and it is in this respect that so many analyses are at fault.

The analyses as made in the Survey Laboratory are more complete than the trade analyses, and though such full analyses are not always necessary, some standard method of analysis, yielding comparable results presented in a similar way, is eminently desirable. It is difficult to obtain an adequate idea of the chemical composition of many silica-rocks from the analyses as furnished by the trade, and in consequence of the incomplete methods of determining the alkalies, soda and potash. These constituents affect the value of the rocks, both by their total amount and by the ratio of one to the other. Their correct estimation is certainly more important than that of silica, which is often erroneously regarded as the only essential constituent. The same remark applies to the estimation of the iron, lime, alumina, and water above 105° C.

The analyses in the following tables have been grouped according to the areas prescribed in Vol. VI of the Special Reports. The arrangement is somewhat arbitrary, for although some of these areas are characterised by rocks of a definite type, belonging to definite formations, in other cases the rocks are of various types and belong to several geological horizons.

The name of the rock, as suggested by a microscopical examination, and applied in accordance with the definitions given in Chap. I, is attached to each analysis.

ANALYSES OF SILICA-ROCKS—GANISTERS AND SANDSTONES.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	XI.	X.	
Lab. No. ...	478	479	482	489	490	491	492	493	494	495	Lab. No.
Slice No. ...	E. 11565	see E. 11565	E. 11566	see E. 11522-3	E. 11520	E. 11519	see E. 11685	E. 11513	E. 11586	E. 11511-2	Slice No.
SiO_2	97·02	82·54	97·91	97·46	98·26	97·59	98·27	98·72	99·03	99·26	SiO_2
TiO_2	·22	·46	·28	·25	trace	·25	·17	·17	·17	·13	TiO_2
ZrO_2	·18	·12	·20	·04	·01	·03	·02	·02	·02	·02	ZrO_2
Al_2O_3	·34	9·10	·17	·55	·35	·38	·60	·65	·51	·28	Al_2O_3
Fe_2O_3	·31	1·33	·38	·59	·56	·37	·14	·10	·09	·10	Fe_2O_3
MnO	·10	·11	·07	·06	·03	·03	nt. fd.	nt. fd.	nt. fd.	nt. fd.	MnO
(CoNi)O ...	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	(CoNi)O
CaO	·05	·14	·07	·16	·19	·08	·01	trace	·01	·02	CaO
MgO	·13	·35	·20	·04	·07	·08	·01	·01	trace	·01	MgO
K_2O	·09	1·11	·06	·10	·14	·15	·27	·14	·12	·08	K_2O
Na_2O	·17	·73	·12	·53	·52	·45	·38	·41	·38	·34	Na_2O
Li_2O	nt. fd.	trace	nt. fd.	nt. fd.	trace	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	Li_2O
H_2O at 105° C.	·02	·89	·02	·05	·03	·05	·01	·04	·03	·04	H_2O at 105°C.
H_2O above ,,	·42	2·77	·37	·20	·30	·42	·47	·24	·09	·09	H_2O above ,,
P_2O_5	·02	·04	·02	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	P_2O_5
FeS_2	·49	·24	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	FeS_2
C	·44	·12	·21	·01	·13	·40	nt. fd.	nt. fd.	nt. fd.	nt. fd.	C.
CO_2	·04	·27	·02	·05	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	CO_2
Total ...	100·04	100·32	100·10	100·09	100·59	100·28	100·35	100·50	100·45	100·37	Total.

ANAL. E. G. RADLEY.

ANALYSES OF SILICA-ROCKS.—DURHAM.

	XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	
Lab. No. ...	516	517	519	520	521	522	523	530	533	Lab. No.
Slice No. ...	E. 11594	E. 11595	E. 11545	E. 11548	E. 11551	E. 11552	E. 11553	E. 11581	E. 11506	Slice No.
SiO_2	98·22	98·20	97·14	95·46	92·61	97·78	96·90	97·16	96·59	SiO_2
TiO_2	·19	·23	·10	·19	·39	·16	·19	·11	·33	TiO_2
ZrO_2	·06	·07	·03	·02	·07	·05	·06	·06	·08	ZrO_2
Al_2O_3 ...	·43	·48	1·12	1·75	1·92	·32	·60	·70	1·56	Al_2O_3
Fe_2O_3 ...	·37	·37	·29	1·01	2·97	·66	1·01	·78	·50	Fe_2O_3
MnO	·02	·03	·04	·07	·02	·04	·04	·11	·05	MnO
(CoNi)O ...	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	(CoNi)O
CaO	·16	·11	·12	·12	·12	·25	·11	·18	·14	CaO
MgO	·04	·09	·08	·13	·30	·03	·03	·15	·08	MgO
K_2O	·07	·07	·35	·10	·15	·09	·12	·21	·24	K_2O
Na_2O ...	·10	·08	·20	·12	·15	·16	·12	·07	·13	Na_2O
Li_2O	nt. fd.	trace	trace	trace	nt. fd.	nt. fd.	trace	nt. fd.	nt. fd.	Li_2O
H_2O at 105°C.	·03	·01	·09	·22	·07	·02	·11	·12	·07	H_2O at 105° C.
H_2O above ,,	·25	·21	·39	·79	1·07	·33	·48	·38	·55	H_2O above ,,
P_2O_5	·02	nt. fd.	nt. fd.	·01	nt. fd.	nt. fd.	·04	nt. fd.	·02	P_2O_5
FeS_2	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	FeS_2
C	nt. fd.	trace	·05	·01	·34	·25	·17	·03	·03	C
CO_2	·14	·08	·03	·06	·06	·02	·05	·04	·04	CO_2
Total ...	100·10	100·03	100·03	100·06	100·24	100·16	100·03	100·10	100·41	Total.

ANAL. E. G. RADLEY.

ANALYSES OF SILICA-ROCKS.—DURHAM—*continued.*

	XX.	XXI.	XXII.	XXIII.	XXIV.	XXV.	XXVI.	XXVII.	XXVIII.	
Lab. No. ...	534	536	537	538	539	540	541	542	543	Lab. No.
Slice No. ...	E. 11510	E. 11590	E. 11591	E. 11592	E. 1152 5	E. 11529	E. 11540	E. 11542	E. 11643	Slice No.
SiO_2	97·47	97·77	98·43	95·51	95·11	97·25	95·65	96·52	97·61	SiO_2
TiO_2	·14	·06	·09	·05	·11	·13	·19	·05	·08	TiO_2
ZrO_2	·07	·02	·08	·06	·04	·09	·08	·10	·02	ZrO_2
Al_2O_3 ...	·70	·26	·39	2·01	1·55	·73	2·15	1·18	·81	Al_2O_3
Fe_2O_3 ...	·41	·34	·31	·47	1·26	·72	·60	·91	·50	Fe_2O_3
MnO	·05	·06	·04	·06	·13	·05	·04	·17	·10	MnO
(CoNi)O ...	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd	nt. fd.	nt. fd.	(CoNi)O
CaO	·19	·13	·12	·18	·19	·22	·17	·23	·17	CaO
MgO	·12	·11	·09	·12	·31	·11	·12	·07	·11	MgO
K_2O	·34	·20	·21	·46	·11	·22	·24	·22	·14	K_2O
Na_2O ...	·27	·18	·10	·24	·29	·12	·09	·17	·19	Na_2O
Li_2O	nt. fd.	trace	trace	trace	trace	trace	trace	trace	nt. fd.	Li_2O
H_2O at 105°C.	·12	·06	·05	·39	·28	·07	·14	·19	·09	H_2O at 105°C.
H_2O above ,,	·28	·45	·08	·44	·65	·32	·64	·41	·22	H_2O above ,,
P_2O_5	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	P_2O_5
FeS_2	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	FeS_2
C	·02	·69	nt. fd.	·05	·06	·03	·04	·04	·03	C
CO_2	·05	·04	·04	·05	·05	·01	·05	·04	·03	CO_2
Total ...	100·23	100·37	100·03	100·09	100·14	100·07	100·20	100·30	100·10	Total.

ANAL. E. G. RADLEY.

I.—*Ganister*, first quality, from No. 1 and No. 3 mines, Main bed, Beely Wood. East side of R. Don, ½ m. S.E. of Oughtibridge. Maps: 1 inch N.S. 100., 6 inch Yorks 288.

II.—*Sandstone*, 'Bastard ganister,' called 'Clay,' from below the Clay Coal, Beely Wood. East side of R. Don, 1 mile S.E. of Oughtibridge. Maps: 1 inch N.S. 100, 6 inch Yorks. 288.

III.—*Ganister*, Wadsley, near Sheffield, Yorks. West side of R. Don. Maps: 1 inch N.S. 100, 6 inch Yorks. 288.

IV.—*Ganister*, below top grit of Third Grit Series. Whiteley's Quarry, Marsden Moor, opposite The Chain Inn, 1½ miles east of Marsden, on South side of main road from Marsden to Meltham. Maps: 1 inch N.S. 86, 6 inch Yorks. 259.

V.—*Sandstone* (Saccharoidal), below top grit of Third Grit Series, Holt Head, near road from Marsden to Meltham, 2½ miles west from Marsden. Maps: 1 inch N.S. 86, 6 inch Yorks. 259.

VI.—*Ganister*, now got beneath 'gob.' Opencast working on crop of Hard Mine Coal, Honley. Near Brook's Dye Works, Gwynn Lane, east of Honley. Maps: 1 inch N.S. 86, 6 inch Yorks. 260.

VII.—Silica Rock. Hard Bed Band Rock. Meanwood Quarry, Bentley. Maps: 1 inch N.S. 70, 6 inch Yorks. 203.

VIII.—*Sandstone*, Guiseley rock, Top lift, Hawksworth Quarry, Windy Ridge, (Hawkstone Hill), one mile S.W. of Guiseley Station, off by-road going from main road from Guiseley to Hawkstone. Maps: 1 inch N.S. 69, 6 inch Yorks. 202.

IX.—*Quartzite* (Saccharoidal), Guiseley rock. Bottom lift. Same locality as VIII.

X.—*Quartzite*, Guiseley rock. First quality. Same locality as VIII.

XI.—*Quartzose Sandstone*, Millstone Grit. West Butsfield Quarry, West Butsfield, Co. Durham. Maps: 1 inch N.S. 26, 6 inch Durham 18 S.W.

XII.—*Quartzite*, Byerley House Quarry, Crook, Co. Durham. Maps: 1 inch 26, 6 inch Durham 18 S.W.

XIII.—*Micaceous Sandstone*, Emerson Peart's Quarry, Lanehead, near Goldhill above Weardale, Co. Durham. Maps: 1 inch N.S. 25, 6 inch Durham 22 N.E.

XIV.—*Sandstone*, Whinstone Quarries, Lunedale, near Middleton-in-Teesdale. Maps; 1 inch N.S. 31, 6 inch Yorks. 4 N.E.

XV.—*Micaceous Sandstone*, Stuartfield Lodge Quarry, Crook, Co. Durham. Maps: 1 inch N.S. 26, 6 inch Durham 18 S.W.

XVI.—*Sandstone*. Same locality as XV.

XVII.— ,, ,, ,,

XVIII.—*Sandstone* (soft), Nattrass Gill, Crook, Co. Durham. Maps: 1 inch N.S. 25, 6 inch Durham 22 N.E.

XIX.—*Sandstone*, Knitsley Fell (Ward's), Wolsingham, Co. Durham. Maps: 1 inch N.S. 26, 6 inch Durham 33 N.W. (not representative).

XX.—*Quartzite*, Harthope Fell, St. John's Chapel, Weardale, Co. Durham. Maps: 1 inch N.S. 25, 6 inch Durham 30 N.E.

XXI.—*Ganister*, Redburn Quarry, Rookhope, near Eastgate, Weardale, Co. Durham. Maps: 1 inch N.S. 25, 6 inch Durham 16 S.E.

XXII.—*Quartzite*, Bounder House Quarry, Crook, Co. Durham. Maps: 1 inch N.S. 26, 6 inch Durham 25 S.W.

XXIII.—*Sandstone* (Carbonaceous), Rookhope, near Eastgate, Weardale, Co. Durham. Maps: 1 inch N.S. 25, 6 inch Durham 16 S.E.

XXIV.—*Sandstone*, Lunedale, near Middleton-in-Teesdale, Co. Durham. Maps: 1 inch N.S. 31, 6 inch Yorks. 4 N.E.

XXV.—*Micaceous Sandstone*, Cross Quarry, Crawleyside, Stanhope, Co. Durham. Maps: 1 inch N.S. 26, 6 inch Durham 17 S.W.

XXVI.—*Sandstone*, Castle Hill Quarry, Castleside, Consett, Co. Durham. Maps: 1 inch N.S. 20, 6 inch Durham 18 N.W.

XXVII.—*Quartzite*, Harthope Quarry, St. John's Chapel, Weardale, Co. Durham. Maps: 1 inch N.S. 25, 6 inch Durham 23 S.W.

XXVIII.—*Quartzite*, Wensley Quarry, near Wensley Station, Yorks. Maps: 1 inch N.S. 41, 6 inch Yorks. 68 N.W.

Analyses of Silica-Rocks,
North-Eastern District.

	XXIX.	XXIXa.	XXX.	
Lab. No.	477	510	511	Lab. No.
Slice No.	—	E. 11489	E. 11491	Slice No.
SiO_2	97·58	97·16	98·15	SiO_2
TiO_2	·65	1·24	·39	TiO_2
ZrO_2	·12	·03	·03	ZrO_2
Al_2O_3	·26	·22	·49	Al_2O_3
Fe_2O_3	·82	·82	·41	Fe_2O_3
MnO	·07	·05	·02	MnO
(CoNi)O	nt. fd.	nt. fd.	nt. fd.	(CoNi)O
CaO	·05	·18	·16	CaO
MgO	·19	·04	·08	MgO
K_2O	·12	·11	·07	K_2O
Na_2O	·14	·02	·04	Na_2O
Li_2O	nt. fd.	nt. fd.	nt. fd.	Li_2O
H_2O at 105° C ...	·01	·02	·01	H_2O at 105°C
H_2O above „ ...	·17	·30	·32	H_2O above „
P_2O_5	·03	nt. fd.	·02	P_2O_5
FeS_2	nt. fd.	nt. fd.	nt. fd.	FeS_2
C	·01	nt. fd.	·04	C
CO_2	·03	·09	·07	CO_2
Total	100·25	100·28	100·30	Total

Anal. E. G. Radley.

Analyses of Silica-Rocks.
Derbyshire.

	XXXI.	XXXII.	XXXIII.	
Lab. No.	481	484	485	Lab. No.
Slice No.	E. 11793	E. 11791	E. 11792	Slice No.
SiO_2	97·99	94·36	96·10	SiO_3
TiO_2	·42	·42	·22	TiO_2
ZrO_2	·15	·14	·19	ZrO_2
Al_2O_3	·32	1·45	·37	Al_2O_3
Fe_2O_3	·31	1·46	1·90	Fe_2O_3
MnO	·09	·13	·09	MnO
(CoNi)O	nt. fd.	nt. fd.	nt. fd.	(CoNi)O
CaO	·04	·11	·15	CaO
MgO	·17	·18	·12	MgO
K_2O	·09	·38	·10	K_2O
Na_2O	·21	·15	·15	Na_2O
Li_2O	nt. fd.	trace	nt. fd.	Li_2O
H_2O at 105° C. ...	·04	·22	·14	H_2O at 105°C.
H_2O above „ ...	·30	·84	·46	H_2O above „
P_2O_5	·02	·02	·02	P_2O_5
FeS_2	nt. fd.	nt. fd.	nt. fd.	FeS_2
C	·04	·12	·09	C
CO_2	·03	·05	·03	CO_2
Total	100·02	100·03	100·13	Total.

Anal. E. G. Radley.

Analyses of Silica-Rocks.
Cheshire and North Staffordshire.

	XXXIV.	XXXV.	XXXVI.	XXXVII.	
Lab. No. ...	509	480	512	547	Lab. No.
Slice No. ...	see E. 11626	see E. 11501	E. 11498	E. 11784	Slice No.
SiO_2	95·16	97·03	98·22	89·60	SiO_2
TiO_2	·47	·07	·19	·52	TiO_2
ZrO_2	·04	·04	·06	·03	ZrO_2
Al_2O_3	2·03	1·61	·44	5·37	Al_2O_3
Fe_2O_3	·41	·38	·37	·75	Fe_2O_3
MnO	·02	·18	·03	·09	MnO
(CoNi)O ...	nt. fd.	nt. fd.	nt. fd.	nt. fd.	(CoNi)O
CaO	·19	·02	·11	·19	CaO
MgO	·07	·11	·07	·14	MgO
K_2O	·35	·14	·13	·53	K_2O
Na_2O	·06	·15	·06	·58	Na_2O
Li_2O	nt. fd.	nt. fd.	nt. fd.	nt. fd.	Li_2O
H_2O at 105° C.	·14	·03	·03	·41	H_2O at 105°C.
H_2O above ,,	1·10	·35	·30	1·53	H_2O above 105°C.
P_2O_5	·03	·02	nt. fd.	·02	P_2O_5
FeS_2	nt. fd.	nt. fd.	nt. fd.	nt. fd.	FeS_2
C	·22	·02	·07	·39	C
CO_2	·07	·02	·06	·02	CO_2
Total ...	100·36	100·17	100·14	100·17	Total.

Anal. E. G. Radley.

Analyses of Silica-Rocks.

	XXXVIII.	XXXIX	XL.	XLI.	XLII.	XLIII.	
Lab. No.	531	535	532	483	486	515	Lab. No.
Slice No.	E. 11582	E. 11587	see E. 4942	E. 11572	—	E. 11585	Slice No.
SiO_2 ...	80·88	93·42	96·44	92·71	74·98	96·87	SiO_2
TiO_2 ...	·65	·52	·07	·22	·83	·03	TiO_2
ZrO_2 ...	·05	·10	·02	·20	·06	·04	ZrO_2
Al_2O_3 ...	9·80	2·69	1·60	3·89	10·33	1·34	Al_2O_3
Fe_2O_3 ...	2·36	·56	·47	·53	4·06	·44	Fe_2O_3
MnO ...	·12	·08	·05	·09	·17	·04	MnO
(CoNi)O ...	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	(CoNi)O
CaO ...	·20	·48	·15	·13	·45	·08	CaO
MgO ...	·31	·08	·06	·09	1·27	·09	MgO
K_2O ...	1·13	·24	·54	·78	2·04	·72	K_2O
Na_2O ...	·38	·21	·13	·18	·25	·24	Na_2O
Li_2O ...	nt. fd.	trace	nt. fd.	nt. fd.	trace	nt. fd.	Li_2O
H_2O at 105° C.	·68	·10	·07	·15	1·44	·06	H_2O at 105° C.
H_2O above 105° C.	2·60	1·10	·48	1·24	3·55	·19	H_2O above 105° C.
P_2O_5 ...	·03	·11	nt. fd.	·05	·21	·01	P_2O_5
FeS_2 ...	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	FeS_2
C ...	nt. fd.	·27	·01	·04	·43	trace	C
CO_2 ...	·85	·12	·07	·02	·04	·04	CO_2
Total	100·04	100·08	100·16	100·32	100·11	100·19	Total.

Anal. E. G. Radley.

Analyses of Silica-Rocks, North Wales.

	XLIV.	XLV.	XLVI.	XLVII.
Lab. No.	513	514	518	529
Slice No.	E. 11575	E. 11625	E. 11596	E. 11636
SiO_2	97·70	98·89	87·85	97·78
TiO_2	·10	·03	·81	·33
ZrO_2	·05	·02	·06	·09
Al_2O_3	1·01	·26	7·08	·68
Fe_2O_3	·47	·31	·63	·44
MnO	·02	·02	·04	·05
(CoNi)O	nt. fd.	nt. fd.	nt. fd.	nt. fd.
CaO	·06	·04	·11	·11
MgO	·05	·05	·05	·03
K_2O	·20	·12	·53	·37
Na_2O	·03	·02	·12	·01
Li_2O	trace	nt. fd.	trace	trace
H_2O at 105° C....	·13	·03	·27	·05
H_2O above „	·36	·17	2·42	·10
P_2O_5	·03	·02	·03	nt. fd.
FeS_2	nt. fd.	nt. fd.	nt. fd.	nt. fd.
C	trace	nt. fd.	trace	trace
CO_2	·03	·07	·07	·05
Total	100·24	100·05	100·07	100·09

Anal. E. G. Radley.

Analyses of Silica-Rocks, South Wales.

	XLVIII.	XLIX.	L.	LI.	LII.
Lab. No.	526	524	525	527	528
Slice No.	E. 11614	E. 11607	E. 11610	E. 11632	E. 11633
SiO_2	98·85	98·14	98·76	97·55	98·07
TiO_2	·03	·33	·06	·39	·39
ZrO_2...	·05	·04	·07	·03	·04
Al_2O_3	·25	·42	·35	·72	·42
Fe_2O_3	·31	·44	·37	·41	·41
MnO...	·02	·03	·02	·03	·02
(CoNi)O	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.
CaO	·04	·11	·04	·02	·06
MgO	·02	·03	·02	·03	·05
K_2O	·07	·10	·16	·23	·15
Na_2O	·13	·11	·03	·12	·17
Li_2O	nt. fd.	trace	trace	trace	trace
H_2O at 105° C. ...	·05	·01	·05	·02	·13
H_2O above „ ...	·17	·19	·21	·41	·09
P_2O_5	nt. fd.	·02	·02	nt. fd.	·03
FeS_2	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.
C	·01	·05	·01	·03	·02
CO_2	·06	·06	·03	·03	·03
Total	100·06	100·08	100·20	100·02	100·08

Anal. E. G. Radley.

XXIX.—*Silica rock*, Lealholm, Cleveland, Yorks. Specimen taken from yard. Maps: 1 inch N.S. 34, 6 inch Yorks. 31 S.W.

XXIXA.—*Sandstone*, Flintoft's Quarry, 2 miles N. of Lealholm, Cleveland, Yorks. Maps: 1 inch N.S. 34, 6 inch Yorks. 31 S.W.

XXX.—*Quartzite*, Castleton Quarries, Cleveland, Yorks. Maps: 1 inch N.S. 34, 6 inch Yorks. 30 S.W..

XXXI.—*Ganister*, Mooredge Mine, Totley, Derby. Maps: 1 inch N.S. 100, 6 inch Derby 17 N.E.

XXXII.—*Sandstone*, Litchfield's Mine, Nether Heage, near Belper, Derbyshire. Maps: 1 inch N.S. 125, 6 inch Derby 40 S.W.

XXXIII.—*Sandstone*, Glossop's Mine, Ambergate, Derbyshire. Maps: 1 inch N.S. 125, 6 inch Derby 40 N.W.

XXXIV.—*Sandstone*, Gun Hill Quarries, Rushton Station, Staffs. Maps: 1 inch N.S. 110, 6 inch Staffs. 4 S.W.

XXXV.—*Sandstone*, Mow Cop, Congleton Edge, Staffs. Maps: 1 inch N.S. 110, 6 inch Staffs. 6 N.E.

XXXVI.—*Sandstone*, Boulton's Quarry, Newbold-Astbury, Staffs. Maps: 1 inch N.S. 110, 6 inch Staffs. 7 N.W.

XXXVII.—*Sandstone*, Furness Vale Fire-clay Works, near Stockport, Cheshire. Maps: 1 inch N.S. 99, 6 inch Cheshire 20 S.E.

XXXVIII.—*Sandstone*, Rishton Colliery, Rishton, near Blackburn, Lancs. Maps: 1 inch N.S. 76, 6 inch Lancs. 63 S.W.

XXXIX.—*Ganister*, Pott Shrigley, near Macclesfield, Cheshire. Maps: 1 inch N.S. 98, 6 inch Cheshire 29 S.W.

XL.—*Sandstone*, Granham's Moor, Pontesbury, Salop. Maps: 1 inch N.S. 152 6 inch Shropshire 40 S.W.

XLI.—*Sandstone*, Cricket Meadow Pit, Upper Gornal. Maps: 1 inch N.S. 167, 6 inch Staffs. 67 S.E.

XLII.—*Silica-rock*, beneath Sandstone. Same locality as XLI.

XLIII.—*Quartzite*. Boon's Quarry, Hartshill, Nuneaton, Warwickshire. Maps: 1 inch N.S. 169, 6 inch Warwickshire 10 N.E.

XLIV.—*Quartzite*, Bwlchgwyn, Minera, Denbigh. Maps: 1 inch N.S. 121, 6 inch Denbigh 28 N.W.

XLV.—*Sandstone*, Crown Dale Quarry, Ffrith, near Wrexham, Denbigh. Maps: 1 inch N.S. 108, 6 inch Flint 17 S.W.

XLVI.—*Sandstone*, Catherall's, Buckley, Flint. Maps: 1 inch N.S. 108, 6 inch Flint 14 N.W.

XLVII.—*Quartzite*, Holyhead Silica Works, Anglesey. Maps: 1 inch N.S. 92, 6 inch Anglesey 5 S.W.

XLVIII.—*Quartzite*, Penwyllt Dinas Co., Craig-y-nos, Brecknockshire. Maps: 1 inch N.S. 231, 6 inch Brecknock 38 S.W.

XLIX.—*Quartzite*, New Quarry, Mynydd-y-gareg, Carmarthenshire. Maps: 1 inch N.S. 229, 6 inch Carm. 53 N.E.

L.—*Quartzite*, A.Y. Dinas Brick & Lime Co., Kidwelly, Carmarthenshire. Maps: 1 inch N.S. 229, 6 inch Carm. 46 S.E.

LI.—*Quartzite*, Brynamman Silica Co., Black Mountain, Carmarthenshire. Maps: 1 inch N.S. 230, 6 inch Carm. 42 N.E.

LII.—*Quartzite*, Quarry at engine-house, near top of incline, Black Mountain Silica Co., Carmarthenshire. Maps: 1 inch N. S. 230, 6 inch Carm. 43 S.W.

ANALYSES OF SILICA-ROCKS—SCOTLAND.

	LIII.	LIV.	LV.	LVI.	LVII.	LVIII.	LIX.	LX.	LXI.	LXII.	LXIII.	LXIV.	
Lab. No.	503	505	544	504	548	501	502	507	508	546	147*	545	Lab. No.
Slice No.	S.19552	S.19555	S.19581	S.19554	S.19613	S.19550	S.19551	S.13724	S.19557			see S.19585	Slice No.
SiO_2	93·49	82·76	85·21	96·08	93·81	95·05	96·26	95·57	86·26	95·21	96·98	98·50	SiO_2
TiO_2	·24	·45	·31	·39	·08	·27	·21	·08	·52	·38	·51	·10	TiO_2
ZrO_2	·03	·03	·10	·04	·03	·01	·04	·02	·02	·04	·08	·04	ZrO_2
Al_2O_3	2·31	10·47	4·73	1·19	·19	1·82	1·34	1·80	5·56	2·26	1·43	·45	Al_2O_3
Fe_2O_3	·74	·57	4·04	·31	·94	·76	·31	·50	1·69	·56	·38	·28	Fe_2O_3
MnO	·04	·02	·23	·01	·12	·02	·03	·04	·18	·06	—	·03	MnO
(CoNi)O	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	—	nt. fd.	(CoNi)O
CaO	1·17	1·22	·20	1·01	1·50	1·13	1·13	1·01	1·31	·23	·18	·20	CaO
MgO	·17	·09	·28	·09	·82	·11	·09	·11	·53	·03	·12	·08	MgO
K_2O	·68	·18	·84	·14	·14	·14	·09	·21	·83	·19	·20	·05	K_2O
Na_2O	·35	·18	·26	·37	·09	·26	·32	·26	1·07	·17	·03	·09	Na_2O
Li_2O	nt. fd.	trace	nt. fd.	trace	trace	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	trace	trace	Li_2O
H_2O at 105°C....	·03	·44	·13	·02	·04	·12	·02	·11	·41	·10	·03	·01	H_2O at 105°C.
H_2O above ,, ...	·60	3·73	1·30	·28	·16	·23	·26	·49	1·49	·88	·44	·17	H_2O above ,,
P_2O_5	nt. fd.	nt. fd.	·08	nt. fd.	nt. fd.	·02	nt. fd.	·02	·02	nt. fd.	—	nt. fd.	P_2O_5
FeS_2	·01	·04	nt. fd.	nt. fd.	nt. fd.	·03	nt. fd.	nt. fd.	·03	nt. fd.	—	nt. fd.	FeS_2
C	·03	·04	·08	·03	·10	·08	·03	·01	·05	·03	—	nt. fd.	C
CO_2	·25	·05	2·27	·05	2·06	·05	·07	·06	·06	·07	—	·04	CO_2
Total ...	100·14	100·27	100·06	100·01	100·08	100·10	100·20	100·29	100·03	100·21	100·38	100·04	Total.

ANAL. E. G. RADLEY.

LIII.—*Micaceous Sandstone*, Bonnybridge, Stirling. Maps: 1 inch N.S. 31, 6 inch Stirling 30 N.W.

LIV.—*Sandstone*, Castlecary, Stirling. Maps: 1 inch N.S. 31, 6 inch Stirling 29 N.E.

LV.—*Sandstone*, Dykehead Fireclay & Ganister Mine, Bonnybridge, Stirling. Maps: 1 inch N.S. 31, 6 inch Stirling 30 N.W.

LVI.—*Sandstone*, 400 yards N.W. of Leemuir, Kilncadzow, 3 miles N.N.W. of Lanark. Maps: 1 inch N.S. 23, 6 inch Lanark 25 N.W.

LVII.—*Sandstone* (*Calcareous*), Underside of Foal Hosie Limestone, Birkwood Burn, Lesmahagow, Lanarkshire. Maps: 1 inch N.S. 23, 6 inch Lanark 31 N.E.

LVIII.—*Sandstone*, Base of Lower Limestone Group, Carb: Limestone Series, Deepsykehead Quarry, between Carlops and Macbie Hill, Peebles. Maps: 1 inch N.S. 24, 6 inch Peebles 5 N.E.

LIX.—*Sandstone*, same Locality as LVIII.

LX.—*Sandstone*, Craigleith Sandstone Quarry, near Edinburgh. Maps: 1 inch N.S. 32, 6 inch Edin. 3 N.W.

LXI.—*Sandstone*, Hermand Old Sandstone Quarry, on east side of Harwood Water, and about ½ mile E. of W. Calder. Maps: 1 inch N.S. 32, 6 inch Edin. 11 N.W.

LXII.—*Sandstone*, East side of stream, 670 ft. E.S.E. of West Houses, Edinburgh. Maps: 1 inch N.S. 32, 6 inch Edin. 8 S.E.

LXIII.—*Sandstone* forming a small cascade, a few feet under (upstream from) No. 6 Limestone in river North Esk, at first bend. S.W. of Kirkettle (old) Mill, half way between Roslin Castle Road Station and Auchindinning Road Station. Maps: 1 inch N.S. 32, 6 inch Edin. 13 N.E. (*Anal. Dr. W. Pollard.)

LXIV.—*Sandstone*, Bankend Farmhouse, ¼ mile N.N.E. of Stevenston Loch, near Smithstone, Ayrshire. Maps: 1 inch N.S. 22, 6 inch Ayr. 11 S.E.

Analyses of Silica-Rocks—Scotland—(*contd.*).

	LXV.	LXVI.	LXVII.	LXVIII.	LXIX.	LXX.	
Lab No.	496	497	498	499	500	506	Lab. No.
Slice No.	S. 19545	S. 19546	S. 19547	S. 19548	S. 19549	S. 19556	Slice No.
SiO_2 ...	95·73	94·64	96·21	93·69	91·68	96·18	SiO_2
TiO_2 ...	·06	·08	·08	·08	·08	·08	TiO_2
ZrO_2 ...	·01	·01	·01	·03	·02	·01	ZrO_2
Al_2O_3 ...	1·42	2·09	1·20	2·07	3·30	1·39	Al_2O_3
Fe_2O_3 ...	·41	·50	·59	·87	·54	·34	Fe_2O_3
MnO ...	·03	·04	·02	·04	·03	·05	MnO
(CoNi)O	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	(CoNi)O
CaO ...	1·37	1·22	1·30	1·26	1·28	·95	CaO
MgO ...	·25	·26	·16	·09	·12	·17	MgO
K_2O ...	·51	·66	·29	1·38	2·47	·22	K_2O
Na_2O ...	·29	·28	·28	·45	·36	·27	Na_2O
Li_2O ...	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	Li_2O
H_2O at 105° C.	·02	·02	·01	·01	·03	·03	H_2O at 105° C.
H_2O above 105° C.	·12	·25	·08	·15	·17	·27	H_2O above 105° C.
P_2O_5 ...	·02	·02	nt. fd.	nt. fd.	nt. fd.	·02	P_2O_5
FeS_2 ...	nt. fd.	nt. fd.	nt. fd.	·06	nt. fd.	nt. fd.	FeS_2
C ...	·01	·03	nr. fd.	trace	·03	·01	C
CO_2 ...	·03	·06	·06	·08	·07	·06	CO
Total ...	100·28	100·16	100·29	100·26	100·18	100·05	Total

Anal. E. G. Radley.

LXV.—*Quartzite*, Shore, a few yards north of N. End of Bonahaven Distillery Buildings, Islay, Argyllshire. Maps: 1 inch N.S. 27, 6 inch Argyll. 187 S.W.

LXVI.—*Quartzite*, Low Shore Cliff, immediately N. of Inver Cottage, Jura, Argyllshire. Maps: 1 inch N.S. 27, 6 inch Argyll. 187 S.E.

LXVII.—*Quartzite*, N.W. Shore of Loch Leven, ¾ mile N.W. of Caolasnacon, Inverness. Maps: 1 inch N.S. 53, 6 inch Inver. 166 N.E.

LXVIII.—*Quartzite*, Laganha "China Stone" Quarry, 1 mile S. of Kentallen, Argyllshire. Maps: 1 inch N.S., 53, 6 inch Argyll. 44 N.W.

LXIX.—*Quartzite*, North east end of Loch Leven, roadside ¼ mile N.E. of Kinlochleven Pier, Inverness. Maps: 1 inch N.S., 53, 6 inch Inver. 167 N.W.

LXX.—*Sandstone* (friable), Argyll Pit, Machrihanish, Argyll. Maps: 1 inch N.S. 12, 6 inch Argyll. 257 S.W.

Trade Analyses of Silica-Rocks.[1]

	LXXXI.	LXXXII.	CLXII.
SiO_2	84·80	89·59	78·000
TiO_2	trace	—	—
Al_2O_3	9·35	6·30	15·500
Fe_2O_3	·77	·86	
CaO	nil	·52	·450
MgO	·19	·55	·036
S	·04	—	—
K_2O	—	·60	·636
Na_2O	·58		
Loss on ignition ...	4·23		
H_2O at 105°C. ...	—	—	—
H_2O above ,, ...	—	1·58	5·700
Organic Matter ...	—	—	
Total	99·96	100·00	100·322

LXXXI.—*Ganister*, Huncoat, Lancs. Anal. E. Riley, London, 1898.

LXXXII.—*White Wormden Stone.* Anal. Thos. Whittaker (Jun.), Accrington.

CLXII.—"*Ganister*," Lower Mountain Mine, Eccleshill. Anal. T. E. Holgate.

	LXXXIII.	LXXXIV.	CXXV.
SiO_2	87·40	78·20	99·28
Al_2O_3	9·83	15·40	·36
Fe_2O_3	—	1·50	·14
CaO	·49	trace	·05
MgO	·57	trace	·04
Alkalies stated as Na_2O	1·71	—	—
Alkalies and loss ...	—	·50	—
Combined water ...	—	4·40	—
Carbonaceous matter, &c.			
TiO_2	—	—	·09
K_2O	—	—	·09
Na_2O	—	—	·05
Loss on ignition ...	—	—	·12
Total	100·00	100·00	100·22

LXXXIII & LXXXIV.—Gillhead Mine, Whitehaven. Anal. Mr. Helton, Whitehaven. (LXXXIII analysed in 1904).

CXXV.—Knitsley Fell Ganister. Anal. W. J. Rees, Dept. of Applied Science, Sheff. University.

[1] Rock-names when given are trade designations and have been supplied with the analyses.

	LXXXV.	LXXXVI.	LXXXVII.	LXXXVIII.
SiO_2	94·20	82·03	94·45	94·20
Al_2O_3	3·29	8·87	2·55	3·29
Fe_2O_3	·81	2·78	·86	·81
CaO	·34	2·06	·63	·34
MgO	·04	·68	·40	·04
K_2O	1·10	·88	·77	1·10
Na_2O				
H_2O	·25	—	—	—
CO_2 and H_2O	—	2·70	—	—
Loss on ignition ...	—	—	·34	·25
Total	100·03	100·00	100·00	100·03

LXXXV.—Hartshill Quartzite, Hartshill Quarry Co., Warwickshire. No. 3 analysis. (Slice No. E. 8053.)

LXXXVI.—Hartshill Blue Stone, Hartshill Quarry. No. 1 analysis. Anal C. Kerslake Baker.

LXXXVII.—Hartshill Granite Quarries, Atherstone (quartzite). Anal. H. B. Bell, F.C.S., A.R.S.M. (April 2nd, 1891).

LXXXVIII.—Windmill Hill Quarries, Nuneaton (quartzite). Anal. W. W. Fisher, F.I.C. (26th July, 1893).

	LXXXIX.	XC.
SiO_2	97·91	96·082
TiO_2	·17	—
Al_2O_3	·77	1·390
Fe_2O_3	·18	1·610
MnO	—	very minute trace.
CaO	·26	·150
MgO	·09	·068
K_2O	·44	nil.
Na_2O		
H_2O at 100° C.	—	·280
Combined H_2O and organic matter.	—	·420
Loss on ignition	·36	—
Total	100·18	100·000

LXXXIX.—Silica Stone quarried at Trevor Rocks, near Llangollen. Anal. Mr. Gibbons.

XC.—Silica Stone. The Bwlchgwyn Roadstone Co., Ltd., Anal. Harry Sylvester, F.I.C., F.C.S., Public Analyst for W. Bromwich.

	XCI.
SiO_2	98·25
Al_2O_3	·74
Fe_2O_3	·34
CaO	trace
MgO	·08
K_2O	—
Na_2O	·11
H_2O at 105° C.	·32
H_2O combined	·15
Total	99·99

XCI.—Cambrian Silica Stone Co., Ffrith, Wrexham (a portion of the same sample, calcined, gave SiO_2=98·71 per cent.) Anal. E. Riley, F.I.C.

	XCII.	XCIII.	XCIV.
SiO_2	99·14	97·74	97·50
TiO_2	·02	·14	—
Al_2O_3	·30	1·01	2·30
Fe_2O_3	·17	·50	
CaO	—	·02	—
MgO	·04	·04	—
K_2O	—	·05	·02
Na_2O			
Loss on ignition ...	—	·50	·18
Total	99·67	100·00	100·00

XCII.—N. B. Allen & Co., Toryfoel Stone. Anal. J. & H. S. Pattensen, Newcastle-on-Tyne.

XCIII.—N. B. Allen & Co., Surface Stone. Anal. J. & H. S. Pattensen, Newcastle-on-Tyne.

XCIV.—Penwyllt Dinas Silica Brick Co., Ltd., "White Bed" No. 6 Quarry. Anal. Morris & Griffin, Newport, Mon.

	XCV.	XCVI.	XCVII.	XCVIII.	XCIX.	C.
SiO_2	94·95	97·68	96·97	98·10	97·50	97·40
TiO_2	—	—	—	—	—	·15
Al_2O_3	1·5	1·13	1·00	1·04	1·4	·20
Fe_2O_3	2·0	·81	·71	·56	1·0	1·40
CaO	1·0	·20	·12	·53	—	·15
MgO	—	—	—	trace	trace	—
K_2O	—	·03	trace	—	—	—
Na_2O	—					
Loss on ignition ...	—	·06	1·16	·10	·5	·70
Total	99·45	99·91	99·96	100·33	100·40	100·00

XCV.—Silica Stone. Blaen Llynfell (blue) Baldwins Ltd. Anal. Chemist to Baldwins, Ltd.

XCVI.—A.Y. Dinas Silica-brick & Lime Co., Kidwelly. Mynydd-y-gareg Stone. Anal. "A Glasgow Chemist."

XCVII.—Another sample of above stone (XCVI.). Same analyst.

XCVIII.—H. & H. E. Smart, Kidwelly. Anal. J. J. Merry, Swansea.

XCIX.—H. & H. E. Smart, Kidwelly. Anal. Wm. Morgan, Swansea.

C.—Lime Firms, Ltd., Llandybie. Anal. C. A. Seyler, Swansea.

	CI.	CII.	CIII.
SiO_2	91·73	93·80	95·50
TiO_2	none	none	·36
Al_2O_3	4·67	4·79	3·38
Fe_2O_3	·79	·81	·05
CaO	trace	trace	·45
MgO	·27	·28	trace
K_2O	·29	·30	·15
Na_2O	trace	trace	·11
H_2O at 105° C. ...	·90	—	—
H_2O combined + organic matter.	1·33	—	—
Total	99·98	99·98	100·00

CI.—Ganister, Bonnybridge Silica & Fireclay Co. Raw material. Anal. Wm. Wallace.

CII.—Ganister, Bonnybridge Silica & Fireclay Co. Burnt material. Anal. Wm. Wallace.

CIII.—Ganister, Jas. Dougall & Sons. Burnt material. Anal. R. R. Tatlock & Thomson.

	CIV.	CV.	CVI.
SiO_2	95·82	96·63	97·76
TiO_2	—	—	·25
Al_2O_3	2·76	1·23	1·17
Fe_2O_3	·08	·06	·08
MnO	—	—	—
CaO	·02	·04	·04
MgO	·01	·02	·04
K_2O	·48	·85	·33
Na_2O	·52	·23	·25
Loss on ignition ...	·65	·58	·38
Total	100·34	99·64	100·30

CIV., CV., CVI.—Three samples of Silica Rock (Sandstone). Drum Pits, Torbanehill, Whitburn. Samples dried at 109° C. Anal. Dr. J. W. Mellor.

	CVII.	CVIII.	CIX.	CX.	CXI.	CXII.
SiO_2	97·28	98·24	98·44	98·45	98·87	99·44
TiO_2	—	—	—	·22	·14	—
Al_2O_3	·91	·95	·92	·39	·27	·26
Fe_2O_3	1·09	·27	·18	·29	·19	·04
CaO	·15	·12	·10	—	—	·04
MgO	trace	trace	trace	·04	·05	·05
K_2O	—	—	—	—	—	—
Na_2O	—	—	—	—	—	—
Loss on ignition ...	nil	nil	nil	·50	·40	·30
Total	99·43	99·58	99·64	99·89	99·92	100·13

CVII., CVIII., CVIX.—Ganister Rock. Cairn Burn, Macbiehill. Analyses communicated by David Colville & Sons, Ltd., Motherwell.

CX.—Waterfall on Cairn Burn, Macbiehill. Anal. Messrs. J. & H. S. Pattensen.

CXI.—About 40 yards below Waterfall, Macbiehill. Anal. Messrs. J. & H. S. Pattensen.

CXII.—Deepsykehead Old Quarry, Macbiehill. Anal. Messrs. J. & H. S. Pattensen.

	CXV.	CXVI.
SiO_2	98·24	98·44
TiO_2	—	—
Al_2O_3	·95	·92
Fe_2O_3	·27	·18
CaO	·12	·10
MgO	trace	trace
K_2O	—	—
Na_2O	—	—
Loss on ignition	nil	nil
Total	99·58	99·64

CXV., CXVI.—Ganister, Cairnburn, Macbiehill, Peebleshire. Anal. D. J. Pinkerton.

	CXIII.	CXIV.
SiO_2	98·17	97·30
TiO_2	·40	·25
Al_2O_3	·87	1·54
Fe_2O_3	·09	·31
CaO	·25	·10
MgO	·01	·01
K_2O	·06	·12
Na_2O	·02	·16
Loss on ignition	·36	·72
Total	100·23	100·51

CXIII.—Ganister, at footbridge in Vogrie Glen, a little below Vogrie House. Anal. Dr. J. W. Mellor.

CXIV.—Ganister on further side of Vogrie Glen, opposite Vogrie House. Anal. Dr. J. W. Mellor.

	CXVII.	CXVIII.	CXIX.	CXX.	CXXI.	CXXII.	CXXIII.	CXXIV.
SiO_2	94·7	96·4	92·4	95·8	95·46	94·76	98·71	97·42
Al_2O_3	1·5	2·05	5·07	·79	1·66	1·84	·52	·94
Fe_2O_3	1·0	·63	1·47	2·21	1·64	2·00	·29	·46
CaO	2·5	1·3	1·0	·9	·90	·90	·31	·40
MgO	·20	trace	trace	trace	·22	·06	·09	·30
K_2O	—	—	—	—	—	—	—	·08
Na_2O	—	—	—	—	—	—	—	
H_2O	—	—	—	—	—	—	·08	
Loss on ignition	—	—	—	—	—	—	—	·38
Total	99·90	100·35	99·94	99·50	99·88	99·56	100·00	99·98

CXVII.—Quartzite, River Orchy, Allt Broighleachan, Argyllshire.
CXVIII.—Quartzite, River Orchy, at upper falls, 7½ miles above Dalmally.
CXIX.—Quartzite, River Orchy, at lower falls, above Allt Broighleachan.
CXX.—Quartzite, Shore, 350 yds. N. of Caol Isla Distillery, Islay.
} Analyses communicated by The Steel Company of Scotland, Blochairn, Glasgow.

CXXI.—Quartzite, West Coast of Jura, 1 mile N. of Inver Cottage, Jura.
CXXII.—Quartzite, a few yds N. of Bonahaven Distillery, Islay.
} Anal. D. J. Pinkerton.

CXXIII.—Sandstone, Machrihanish, Campbeltown, Argyllshire ... ... ? Analyst.
CXXIV.—Quartzite, east shore of Sound of Islay, N. of Inver Cottage, Jura Anal. Wallace & Clark.

	LXXI.	LXXII.	LXXIII.	LXXIV.	LXXV.	LXXVI.	LXXVII.
SiO_2 ...	98·55	99·20	98·60	97·60	97·58	97·48	97·05
TiO_2 ...	—	trace	·15	·19	—	—	—
Al_2O_3 ...	1·00	·34	·45	1·14	1·02	·94	1·35
Fe_2O_3 ...	trace	·14	·40	1·57	·13	·24	
MnO ...	—	—	—	—	—	—	—
CaO ...	·11	·15	·20	·10	·21	·18	—
MgO ...	·25	·10	·10	·16	·14	·11	—
K_2O ...	—	trace	trace	·05	·29	·17	—
Na_2O ...	·18	·05	·08	·12	·30	·31	—
H_2O at 105° C.	—	—	—	—	·35	·50	—
H_2O above 105° C.	—	—	—	—	—	—	—
Loss on ignition.	—	·51	·69	·92	—	—	—
Total ...	100·09	100·49	100·67	101·85	100·02	99·93	—

LXXI.—Ganister from Castleton, Cleveland, Yorks. Communicated by A. L. Stevenson, Esq.

LXXII.—Ganister from Byerley House Quarry, near Satley, Co. Durham. Anal. Dr. Stead.

LXXIII.—Stone from Stuartfield Lodge Quarry. Anal. Dr. Stead.

LXXIV.—Stone from Cross Quarry, Crawleyside, near Stanhope, Co. Durham. Anal. Dr. Stead.

LXXV., LXXVI., LXXVII.—Three samples of "Firestone" or "Ganister" from Messrs. Wm. Benson & Son's Quarry, at Fourstones, near Hexham.

	LXXVIII.	LXXIX.	LXXX.
Insoluble SiO_2 ...	79·30	81·10	87·74
Soluble SiO_2	7·46	7·63	6·03
TiO_2	—	—	—
Al_2O_3	5·96	6·09	5·11
Fe_2O_3	1·23	1·26	·33
MnO	—	—	—
CaO	1·54	1·58	·14
MgO	·40	·41	·13
K_2O	1·20	1·22	·24
Na_2O			
Loss on ignition ...	2·22	—	—
Sulphates	·69	·71	—
Sulphur trioxide ...	—	—	·28
Total	100·00	100·00	100·00

LXXVIII & LXXIX.—A bed that occurs as a "ripping" above the Tupton Coal. Messrs. Oakes & Co.'s Colliery. (LXXVIII, dried; LXXIX, burnt). Anal. J. T. Norman.

LXXX.—"Ganister" from Messrs. Swann, Ratcliffe & Co., Ltd., Brassington. Analysis supplied by Messrs. J. Oakes & Co., Ltd., Riddings Colliery & Brickworks, Pyebridge, near Alfreton.

CHAPTER IV.

Discussion of Silica-Rock Analyses.

A study of the analyses given in Chap. III reveals certain facts which are worthy of emphasis and discussion.

The main points to which attention should be directed are the mutual dependence and relative proportions of certain constituents of the rocks in question, more especially of the alumina, the alkalies, and of the combined water given off above 105° C., and consideration of the relation of the contained lime to alumina and carbon dioxide.

The analyses of the various types of silica-rocks show that considerable differences of composition exist. The silica, for instance, in some of the more highly silicified rocks of the Millstone Grit of Yorkshire, reaches a percentage of a little over 99, in the ganisters it averages about 98, while it falls in the quartzose sandstones to as low a figure as 80. This fall in silica is generally accompanied by an increase in the percentage of alumina, alkalies, and combined water.

The rocks of certain districts and of certain geological formations have fairly constant compositions, and therefore a comparison of the analyses of the rocks of different areas and different formations becomes instructive.

The ganisters of the Sheffield district, rocks that occur in the Lower Coal Measures, possess remarkable uniformity not only in macroscopic and microscopic characters, but also in chemical composition. The silica content is generally from 97 to 98 per cent., with an average of about 97·7. The percentages of the other constituents are necessarily small, but present two striking features in the low proportion of alumina, which averages about 0·35 and seldom reaches 0·5 per cent., and the constant excess of soda over potash. The alkalies, taken together, hardly ever reach 0·65 per cent. and usually the amount of soda is twice that of the potash, the average being potash 0·14 and soda 0·28 per cent.

In addition to the above, the analyses of the ganisters prove a general absence of carbonates, and a relatively low percentage of hydrated silicates as indicated by the combined water.

The ganisters of the Millstone Grit of the Sheffield area are remarkably similar to the Coal Measure ganisters, but contain a slightly higher percentage of silica, averaging about 98·5, and relatively higher alumina with an average of about 0·47 per cent., while, with a small increase in the total percentage of alkalies, the excess of soda over potash, which was noted in the Coal Measure ganisters, is accentuated, being in the ratio of 3 or 4 to 1.

The ganisters of Durham and the North Eastern areas as well as those of Derby, and the ganister-like quartzites, have, in general, a slightly higher percentage of compounds other than

silica, or what may be termed 'impurity.' Compared with the Yorkshire ganisters, the percentage of alumina increases, while that of the alkalies remains about the same, but as a general rule the soda is not in excess of the potash, the alkalies being either in about equal proportions or with an excess on the side of potash.

Turning to the so-called 'ganisters' of Scotland, which would be better described as ganister-like carbonaceous quartzose sandstones, we notice a considerable diminution of the silica-percentage and a consequent increase in the other constituents. The silica-content of these rocks, which is fairly constant, averages about 95 per cent. The alumina is higher than that in the majority of English ganisters, sometimes reaching 2 per cent., while lime and carbon dioxide and combined water are present in relatively greater amounts.

The quartzites such as those of Holyhead in Anglesey, Islay, Jura and other localities in Scotland, as well as some of the silicified rocks belonging to the Millstone Grit of Wales, show divergence amongst themselves, both microscopically and chemically. The Scottish quartzites, compared with the ganisters, show a reduced silica-percentage, averaging about 94·4, but higher alumina and lime and potash, with potash invariably in excess of soda. The English and Welsh quartzites of the older geological formations are represented by those of Hartshill and Holyhead respectively. These differ somewhat widely in composition, the Holyhead rock comparing more closely with some of the ganister-like Carboniferous sandstones and with the Pennsylvanian quartzite of the United States, while the Hartshill quartzite, in its lower silica and higher alumina and potash, resembles some of the less highly silicified quartzose sandstones of the Millstone Grit.

Rocks that cannot be classed with the ganisters, but that cannot be well described under any other name than quartzites, occur in the Millstone Grit series of North and South Wales, in the Millstone Grit of Yoredale and the Carboniferous Limestone Series of the North of England. Again the Moor Grit in the Jurassic rocks of the Cleveland district is of similar character. Many of these come exceedingly close in composition to true ganisters, while others, through gradual stages, approach more nearly the sandstones and show the same type of variation.

Generalisations on the chemical composition of quartzites are difficult, for each rock must be treated on its merits, and with regard to its microscopic structure and mineral composition. Many quartzites, however, have proved satisfactory and are being used for the manufacture of silica-bricks.

The sandstones, as might be expected from their variable nature and degree of cementation, yield widely different chemical analyses. The more or less pure quartz-sandstones, composed of closely-packed grains and having little interstitial matter, even if feebly cemented, give analyses that differ but little from those of good ganisters, while a compact, firmly cemented rock may show a composition indicative of the presence of a large percentage of material other than quartz.

The silica-percentage of the usable sandstones is generally lower than that possessed by the ganisters and quartzites, falling

in some instances to below 80. The alumina is higher than that of the ganisters, occasionally rising to as much as 90 per cent., and at the same time there is a rise in the percentage of alkalies, more particularly of potash, and occasionally a relatively large rise in the percentage of combined water.

In special cases a percentage of carbon dioxide, higher than that usually found in the ganisters and quartzites, is accompanied by an increase in the percentages of one or both of the oxides, CaO, MgO.

To illustrate the above points, the analysis of a quartzose sandstone of some purity (No. XVIII.) is tabulated alongside analyses of the less pure sandstones Nos. LIII., LV., and II.

	XVIII.	LVII.	LV.	II.
SiO_2	97·16	93·49	85·21	82·54
Al_2O_3	·70	2·31	4·73	9·10
Fe_2O_3	·78	·74	4·04	1·33
CaO	·18	1·17	·20	·14
MgO	·15	·17	·28	·35
K_2O	·21	·68	·84	1·11
Na_2O	·07	·35	·26	·73
H_2O	·12	·60	1·30	2·77
CO_2	·04	·25	2·27*	·27

* This CO_2 is combined with FeO in the form of ferrous carbonate.

The rise in the percentage of alumina and the attendant rise in the amount of K_2O and combined water are well exemplified. Their significance is discussed below.

For the purpose of considering how far the chemical analyses of silica-rocks can be interpreted in terms of their mineralogical compositions, it will be well to review each principal constituent and to enquire how, and to what extent, it may be combined with other constituents to form compounds known or inferred to be present in the rock as component minerals.

Silica.—Of this constituent a variable proportion, which increases as the total silica percentage diminishes, is combined to form aluminous or non-aluminous silicates such as the felspars, muscovite, and kaolinite. Out of a total percentage of 97·7 of silica probably not more than 1·1 per cent. exists in a state of combination, but with a low percentage, say 74, the proportion of combined silica increases, leaving only between 60 and 65 per cent. in the pure condition as quartz.

Alumina.—Usually the alumina of silica-rocks is either combined with alkalies and silica to form felspars, or with potash, silica, and water as white mica (muscovite), or with water and silica alone in the form of kaolinite or some allied hydrated aluminium silicate. Without microscopic study, the best guide to the form of combination is the relative percentage of combined water (above 150° C), considered in connexion with the amount of alkalies. Relatively high percentages of alumina and potash, coupled with a low percentage of combined water, point to the presence of potash felspar, while the same percentage of alumina, with proportionately more potash and water, suggests the presence

of muscovite. On the other hand, a high alumina-content, with low potash and a still higher percentage of water, prove more or less conclusively the existence of kaolinite or some similar clay-mineral. This matter will be further considered under the heading of the alkalies (*see* below).

Lime.—As the only phosphate likely to be present in silica-rocks is calcium phosphate, any P_2O_5 found by analysis must be satisfied by an equivalent of CaO, and this deducted from the total. The remaining lime, if any, may be combined with carbon dioxide to form calcite, or, with the addition of magnesia, to form dolomite. It is occasionally found that the amount of lime present is satisfied by CO_2 and P_2O_5, but in other cases there is an excess over that needed to form the compounds named above, and then such excess is best regarded as being in a state of combination with alumina and silica with some soda, in the form of a soda-lime or plagioclase felspar.

Magnesia.—This constituent seldom, if ever, reaches as much as 1 per cent., for ferro-magnesian silicates or hydrated magnesian silicates, such as serpentines, are seldom met with and even carbonates are of rare occurrence. When, however, the percentage of magnesia mounts above the average, it is usually accompanied by a corresponding rise in that of the carbon dioxide. This points to the presence of dolomite, as, for instance, in a certain Scottish ganister, in which the CO_2 is 2·06 the MgO is 0·82 and the CaO 1·50, a set of figures which indicates the existence of calcite with a subordinate amount of dolomite.

Potash.—The potash is combined either with alumina and silica to form the anhydrous mineral, orthoclase felspar, or with the same constituents, together with water, to form muscovite. In practically every case there is sufficient alumina to satisfy the potash, on the supposition that these constituents are combined as orthoclase. There is often, however, especially in the less pure rocks, an insufficiency of potash compared with alumina if orthoclase is to be regarded as the dominant potash mineral. Under these circumstances, the rock will probably contain a greater percentage of combined water than usual, a state of things which indicates the presence of muscovite. In muscovite, the potash enters into combination with about three times as much alumina as in orthoclase.

Soda.—In most rocks soda is found to be combined with alumina and silica in the ratio:—$Na_2O : Al_2O_3 : SiO_2 = 1 : 1{\cdot}65 : 5{\cdot}8$ to form the plagioclase felspar, albite, and there is no doubt that in many cases this mineral is also a minor constituent of silica-rocks. In the analyses made in the Geological Survey laboratory great care has been exercised in the estimation of the alkalies, and although soda, as a general rule, occurs only in fractions of 1 per cent., there is often an excess over and above that necessary to satisfy the alumina not required by other mineral combinations. The variation in the percentage of potash finds expression in a corresponding variation in the mineral constituents, which can be detected with the aid of the microscope, but variations in the soda-percentage, except in the very few cases in which plagioclase felspar can be identified, do not appear to be

accompanied by any noticeable change in the mineral composition of the rock. The excess of soda, although small, is particularly conspicuous in those rocks which have undergone extensive secondary silicification, such as the true ganisters and the ganister-like sandstones of the Millstone Grit. We are forced to the conclusion that this excess of alkali exists combined with silica as a hydrous sodium silicate in the interstitial and cementing secondary silica. The silica which now forms the cement of these rocks was probably introduced by an alkaline solution and, therefore a retention of a slight excess of alkaline silicate is to be expected. This suggestion finds confirmation in the fact that opaline silica often contains as much as 1 per cent. of soda without any alumina being present, and that sodium silicate has been detected as liquid inclusions in crystalline quartz.

Combined water.—The water given off above the temperature of 105° C, must be considered as entering into the composition of one or more of the hydrous minerals usually present in rocks of this character. Its percentage, in the silica-rocks, is variable, ranging from below 0·1, to about 1 per cent. in the case of the quartzites and more highly silicified sandstones, and from this figure to as much as 3·5 per cent. in the case of the sandstones, the percentage rising as the degree of impurity increases.

In rocks with a moderately high percentage of Fe_2O_3 and combined water, some of the latter may be in combination with ferric oxide in the form of limonite or one of the other hydrated oxides of iron, but the percentage so combined must be small, as 1 per cent. of water requires nearly 6 per cent. of ferric oxide to form the commonly occurring oxide, limonite.

The microscope, or even a study of the hand-specimens of sandstones, will generally reveal the presence of muscovite, and kaolinite may be detected as soft white spots in many of the sandstones and less completely silicified members of the Millstone Grit Series. In highly silicified rocks, however, except perhaps in the case of the older quartzites, mica occurs in such an extremely fine state of division that its presence is not easily discernible. It probably exists as minute flakes, formed by the decomposition and hydration of orthoclase felspar. Such mica will account in many instances for all the combined water found by analysis, but in other cases, more especially in the less purely siliceous rocks, the combined water reaches such a figure that if it all entered into the constitution of muscovite the rock would have to possess a much greater percentage of potash than that actually found.

After allowing for the combined water in any hydrated oxide of iron that may be present, for the alumina and potash to form orthoclase, and for alumina, potash, and water in the proportion requisite to form muscovite and to satisfy completely the potash found by analysis, there often remains an excess of both alumina and water which, together with silica, forms kaolinite or some allied hydrous aluminium silicate. This is particularly noticeable in such rocks as those represented by analyses Nos. II and LV quoted above when dealing with the alumina-percentages.

Carbon Dioxide.—This constituent, evolved on the addition of acid, can only exist in the form of carbonate, either combined with lime as calcite, or with lime and magnesia as dolomite, or in some cases with ferrous iron as chalybite. The ratio of CO_2 to CaO in calcite is approximately 1 to 1·27 and of CaO to MgO in dolomite, 1 to 1·1. From this it is easy to see whether the lime and magnesia in any analysis are completely satisfied by CO_2 or whether there is an excess of these oxides left over to form lime felspars or ferro-magnesian silicates. In some instances the percentage of CO_2 is more than is required by the total lime and magnesia, and the excess of CO_2 must then be in a state of combination with ferrous iron, which, owing to the usually small amount of iron found, has been included in the total iron estimated as Fe_2O_3. Such a case is that furnished by analysis No. LV, in which the 2.27 per cent. of CO_2 obviously cannot be satisfied by a total lime and magnesia of 0·48 per cent.

Ferric Oxide.—All the iron of these silica-rocks has been estimated as ferric oxide, but some iron may be present in the ferrous state. The microscope seldom reveals any of the anhydrous oxides of iron such as magnetite and hæmatite or the titaniferous iron ores, titanomagnetite and ilmenite. It is probable therefore, as is indicated by the staining noticeable on the joints, and even in the body of many silica-rocks, that the iron exists mostly in the state of some hydrated oxide. In certain instances, the presence of some ferrous carbonate is proved by the microscope and by the analysis of the rock in question, the analysis showing a greater percentage of CO_2 than can be satisfied by the lime and magnesia.

Titanium oxide (TiO_2).—The titanium as found by microscopic examination of the silica-rocks and of their insoluble residues, is present in the form of oxide, generally as rutile, and less frequently as brookite or anatase. Rutile most often occurs as minute detrital crystals in the interstitial material, and the same is true, but to a less extent, of anatase. Brookite, however, although occasionally occurring in relatively large detrital flakes, most often builds minute secondary crystals which are embedded in the cementing silica of many ganisters and ganister-like sandstones, especially those of Yorkshire and Durham. (Plate I, Fig. 6.)

With a high silica-percentage, the TiO_2, usually below 0·3 per cent., is mainly in this form, but in the less pure and less silicified rocks in which the interstitial material is of greater amount, most of the titanium is present in the form of detrital rutile (*see* analyses Nos. LXI, LXIII, XXXVIII, XXXIX).

The secondary brookite was probably deposited with the cementing silica, and was carried by the same alkaline solution.

Zirconia.—This compound exists only as zirconium silicate (zircon), a mineral of extreme durability and one that occurs in most sedimentary rocks as detrital grains or minute crystals.

Phosphoric anhydride.—In all rocks of this nature P_2O_5 is combined with lime to form the mineral apatite which, like zircon, is detrital in origin. The ratio of P_2O_5: CaO in apatite is as 1 : 1·18.

Iron pyrites (FeS_2).—This mineral is of rare occurrence in any quantity as an evenly distributed constituent of the silica-rocks. In small quantities it has been detected in the Guiseley Rock (analyses I and II), in certain Scottish sandstones (analyses LIII, LIV, LXI), and in the quartzite from Kentallen, Argyll, (analysis LXVIII).

Pyrites may have been originally present in most of the rocks that contain iron, but, if so, it has been oxidised with the loss of sulphur to ferric oxide.

Carbon.—The obvious carbonaceous streaks and patches of the ganisters and of many ganister-like sandstones, suggest that these rocks might contain a fair percentage of carbon, but it is surprising to find how small this percentage usually is. The dark colour of the rock is misleading, and it is clear that, as a pigment, carbon in a fine state of division produces effects out of proportion to the quantity present. Even in those ganisters which appear to be the most carbonaceous, the percentage of carbon seldom rises above 0·5. Generally it is much lower, and in one instance only, to our knowledge, does it reach the high figure of 0·69 (analysis No. XXI).

CHAPTER V.

The Effect of Impurities and Structure upon the Softening-point of Silica-Rocks.

When heated with more or less rapidity to temperatures approaching 1,700° C., all silica rocks show signs of losing their rigidity and of passing into a state of fusion. The temperature at which this change begins is no doubt governed by the chemical composition of the rock, but the extent to which it becomes evident is dependent both on the chemical composition and on the texture of the rock. At these temperatures quartz is converted almost as rapidly as it melts into cristobalite, which has a much higher melting-point, and it is only when the fusion becomes more rapid than the conversion that this temporary melting becomes obvious. The true melting-point of quartz is therefore difficult to observe.

Pure substances theoretically melt at a constant temperature, and the change of state from solid to liquid on a temperature-time curve will be represented, as in the curve for pure silver shown on the left in Fig. 1, by a horizontal line of constant temperature, its length indicating the time taken for the substance to change completely from the solid to the liquid state, under the influence of a uniform supply of heat.

It is found, however, that the melting-curves of the majority of pure silicates are less simple and present a general obliquity, some much more than others, instead of the horizontal section that represents a change of state at constant temperature. This behaviour of the silicates and the apparent extension of their melting-points over a considerable range of temperature is due to two main causes, firstly to a time-lag in the melting process, connected with the extreme viscosity of the substance near its true melting-point, and secondly, in the presence of impurity, to depression of the melting-point; this depression is commonly proportional to the amount of impurity and is very important in the case of refactory substances. For silica, however, the depression of the freezing-point (the temperature at which the melted material begins to deposit pure silica) by impurities appears to be exceptionally small, and so this effect, though of the highest importance in refractories subjected to prolonged heating, is liable to be completely masked on rapid heating by the delay due to viscosity.

The viscosity of silica at and near its melting-point is well-known. The plagioclase felspars present this character in a still more marked manner, as shown by the investigations of Messrs. Day and Allen.[1]

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[1] The Isomorphism and Thermal Properties of the Feldspars, Washington, 1905.

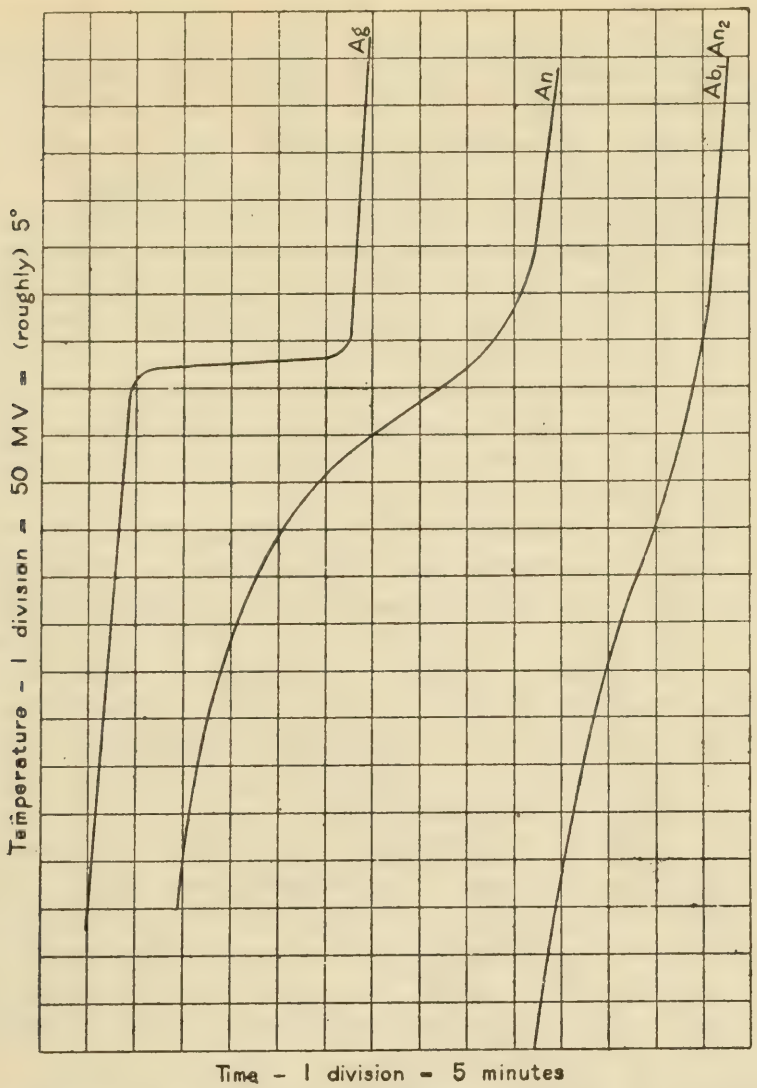


FIG. 1.—Time-temperature cooling curves of Silver, Anorthite and a Soda-lime Felspar (Ab_1 An_2), showing delayed crystallisation of the felspars as compared with Silver.

Typical curves obtained by these workers are reproduced in Text-Fig. 1, the curve for pure silver having been determined also for comparison. The melting-range of the felspars, extending over as much as 50° C., contrasts strongly with the sharply defined melting-point of silver. For the lime felspar (anorthite) the results bear some resemblance to the normal curve, the heat evolution on cooling being concentrated within a fairly limited range. As the mixture approximates in composition to the soda felspar (albite) the heat-evolution becomes more extended and the curve gives less indication of a decisive melting-point, till in the case of albite itself the position of the melting-point becomes quite indeterminate. Micro-sections of the preparations give interesting information as to the nature of the delay. Quite apart from the existence of the melting-range always found during the crystallisation of a mixture, two distinct effects can be traced. First, there is a definite lag (supercooling) due to the slow rate of crystallisation. With mixtures of albite and anorthite ranging in composition from pure anorthite to Ab_1 An_1 the micro-sections show a completely crystalline structure; the whole of the latent heat of fusion has therefore been evolved on solidification and the curve is simply a normal curve in which

the horizontal or oblique displacement representing heat-evolution has been distributed over a considerable temperature-range. For mixtures containing more than 50 per cent. of albite a second effect intervenes. The rate of crystallisation is so slow in comparison with the rate of cooling that crystal-growth is arrested before the heat-evolution is complete, the remainder of the melt being found as a glassy residue between the distorted and spherulitic crystals. In this case freezing is more or less completely eliminated; in the extreme case, that of albite, it does not appear that any of the latent heat of crystallisation could have been evolved, and the cooling-curve shows no feature to correspond with the melting-point of the substance. The same sluggishness of transformation was found to affect the formation of melt from the crystalline phase on heating.

From this short summary of the behaviour of the felspars it will readily be understood that silica, which is quite comparable with them both in viscosity and slowness of transformation, may well show rigidity at temperatures far above its true melting-point, provided that the rate of heating is sufficiently rapid. The speed of cooling of the furnace corresponding with a supercooling of about 50° for anorthite is approximately 5° per minute, and this is a value comparable with that given in the specification for silica-rocks to be discussed below.

In the standard specifications for refractory materials it is set out that in a furnace, the temperature of which is raised at the rate of 50° C. in 5 minutes, material that contains 92 per cent. and upwards of silica should show no sign of fusion when heated to Seger cone 32 (about 1,710° C.), and that material with from 80-92 per cent. of silica should similarly remain unaffected up to Seger Cone 29 (about 1,650°C.).

For those silica-bricks in which much of the quartz has been converted into other modifications of silica, this test may be of some value because of the higher and better defined melting-points of those modifications, but in the case of silica-rocks the test appears to us to be of no practical utility. We know that, given sufficient time, quartz liquefies completely at 1,625° C., and if the rock shows no signs of fusion at 1,710° C., this must be due either to the rise of temperature having been too rapid to allow the viscosity of the silica near its melting-point to be overcome and the fusion to make itself apparent, or else to the formation of a layer of cristobalite which concealed the fusion of the unconverted quartz. It is, therefore, not surprising to find that tests such as these when applied to silica-rocks, which mostly contain over 92 per cent. of silica, demonstrate the fact that rocks of various composition, and which cannot be regarded as of equal desirability, behave in an apparently identical manner. All that can be learned from them is that rocks with a high percentage of alumina and combined water soften more readily than others in which these constituents are less strongly represented.

The effect of rapidly heating most silica-rocks to their obvious softening-points (about Seger Cones 34-36) is to reduce them to silica-glass, which contains in most instances vesicular cavities. These are formed mainly by water vapour evolved by the decomposition of hydrated minerals, such as kaolinite, muscovite, etc., and in this connexion it is to be noted that rocks with the lower

softening-points usually furnish the more vesicular products. The softening of a silica-rock, at a temperature below the softening-point of the form of silica present, is due to compounds other than silica, and, as we have seen, these usually occur as interstitial matter, but are sometimes present as separate mineral grains. Obviously, therefore, the texture of the rock must affect the softening-point, for any segregation of impurities in local patches will be accompanied by local softening, while uniformly distributed impurity will produce a softening effect throughout the whole mass. Again, the form of the grains will also play a part, for it is certain that a rock composed of interlocking angular grains, though containing interstitial fluxing matter, will retain its rigidity to a higher temperature than one in which the grains are rounded and freer to move.

Such considerations as the above, especially the viscosity of silica and many silicates at or near their melting-points, explain why the majority of silica-rocks show no definite signs of fusion at such high temperatures as are indicated by the Seger Cones 35 and 36 (1,770°-1,790° C.).

The most recent determinations of the melting-points of tridymite and cristobalite are 1,670° C. and 1,710° C. respectively, according to Ferguson and Merwin in 1918. The rate of conversion of quartz into the higher-temperature modifications of silica being extremely slow, the tests as carried out do not allow time for more than partial conversion. The melting-point of quartz is probably reached before any great quantity of this mineral has suffered conversion. Quartz, heated slowly, begins to change into the form of cristobalite at about 1,250° C. and the change becomes more rapid and complete at and above 1,470° C. On complete conversion the melting-point will be that of cristobalite, 1,710° C. as compared with the melting-point of quartz about 1,600° C. Thus if heated with sufficient slowness to ensure more or less complete conversion, it is probable that the more siliceous silica-rocks will remain rigid far above the melting-point of quartz.

For practical purposes, therefore, the softening of silica-rocks, when used as refractories, may be regarded as being independent of the melting-points as observed on rapid heating; it is governed rather by the temperature of formation, quantity and degree of mobility of the interstitial fluxes. The compounds entering chiefly into those fluxes are silica, alumina, lime, iron, and the alkalies, and these are supplied by such minerals as the alkali and soda-lime felspars, kaolinite, muscovite and limonite. In these fluxes silica is soluble to a greater or less extent and will separate out on cooling as cristobalite or tridymite, according to the temperature and concentration.

The first step in the formation of fluxes is probably the fusion of some mineral with a low melting-point which brings about the liquefaction, either by solution or combination, of other constituents of the rock. It is obvious that combinations are effected in the interstitial portion of silica-rocks which would only take place at temperatures beyond those of the usual ranges of firing, unless some such intervention is assumed.

It must not be taken for granted, as has often been done, that the melting-point of a silicate is the temperature at which the

silicate will be formed on bringing together its constituent oxides; the temperature of formation of a compound is sometimes higher than its melting-point. Nevertheless, in dealing with silica rocks that have been heated at the firing temperature for the full period, and with bricks from the furnace, it may be assumed with fair certainty that the chemical equilibrium of the interstitial melt has been attained.

The low melting-point of the alkali felspars suggests that these substances will be the first to undergo fusion, the resulting liquid having the power of dissolving silica and aluminous compounds, in amounts which vary according to the temperature.

The alkali felspars melt at temperatures between 1,100° and 1,200° C., and it is interesting to note that at a temperature of 1,460° C. fused orthoclase is capable of dissolving its own weight of silica. It is, therefore, a fair assumption that the fluxes which are primarily responsible for the softening of silica-rocks are of an alkaline nature and originate in the alkaline felspars.

Kaolinite at an elevated temperature dissociates into aluminium silicate and free silica, both of which will dissolve in fused alkaline silicates with the separation of crystalline sillimanite from the melt. Muscovite dissociates slowly in a similar manner, probably into the form of amorphous orthoclase and alumina, which can enter into the constitution of any fluxes already present. The final amount of flux, must, therefore, be influenced by the percentage of aluminous material present in the rock.

Calcium carbonate will flux with silica at a relatively low temperature, the ortho-silicate forming between 1,400° C. and 1,500° C. from the lime and silica. On continued heating this silicate absorbs more lime and passes into the tricalcic and the meta-silicate. Advantage of this reaction is taken in the manufacture of silica-bricks in which lime is added to the material before firing. In the presence of a silicate-melt this combination will be effected at a lower temperature, and the same probably holds good for magnesia when in the form of magnesium carbonate.

Iron compounds, particularly the oxides, are readily soluble in fused silicates with the formation of iron silicates of low melting-points. Any ferro-magnesian silicates and basic plagioclase felspars are soluble in silicate-melts but only at relatively high temperatures. Moreover, they seldom exist in silica-rocks in sufficient quantity to play an important part in the initial formation of fluxes.

From the foregoing it is clear that the softening of a silica-rock determined on rapid heating in the laboratory depends upon a variety of causes, among which the chief factors are the mineralogical composition and physical structure. On the other hand, when the rock is heated for a long period at the highest temperatures, these have but little influence on the refractory properties; even in the kiln the original minerals are completely dissolved in the interstitial melt of which the amount formed depends simply upon the chemical composition, the sole exception being that the form of the quartz-grains may still modify the strength of the ganister-fragments, and so affect the strength of the brick as a whole. The measurement of the softening-point on rapid heating is therefore of doubtful value, whether it be regarded as a test of the refractory character or of the chemical purity of the rock.

CHAPTER VI.

Silica-Bricks.

Introduction.

It will be seen in the following chapters that the variety of properties required in silica-bricks results in many conflicting demands being made on the manufacturer. The quality of the brick is the product of many opposing factors, and between these a choice must be made according to the purpose for which the brick is to be used. Perhaps the most conspicuous instance is the difficulty of combining adequate density with the elimination of permanent expansion. For the steel furnace the relatively dense brick would appear to hold the field, but for many purposes where corrosion by slagging is no longer the main factor in durability it becomes possible to give fuller attention to the elimination of expansion; this is especially true of bricks for coke ovens. The manufacturer must therefore consider the purpose for which his bricks are to be used, and no single specification can be made to cover all the varied types needed. This has not been fully realised, and confusion has been caused by the assumption that the elimination of expansion is to be the main object of the brick-maker.

In the following pages an attempt will be made to indicate the effect of variation in each physical property upon the value of the brick. It must be borne in mind that control of the process of manufacture is by no means fully developed. An attempt to improve one quality is apt to lead to deterioration in another, as, for example, when an increase in density is nullified by the development of spalling. But some advantage can generally be obtained by careful work towards the elimination of minor defects provided that the object in view is clearly specified.

The process of manufacture, although generally similar both at home and abroad, differs in detail from place to place. The main differences met with are connected with the composition and texture of the silica-rock employed, the method of crushing and grinding, the nature and amount of material added to form a bond, the method of moulding, and lastly the temperature and duration of firing. As regards the British manufactures, several of these differences have been discussed in Chapter I, but it may be well to consider some of them more fully, especially those connected with the raw material, the bond and the firing.

The Raw Material.

Quartzites and siliceous sandstones that offer a considerable variation in both composition and texture are used for the manufacture of silica-bricks, but it is essential that they should possess granular structure and a high percentage of silica coupled with a low percentage of alumina and alkalies. The preparation of a

brick of a specific refractory nature, with the requisite density, strength, porosity and durability, is connected on the one hand with these characters, and on the other hand with the nature and amount of the added bonding-material. The production of the bond is aided, as will be shown, by the interstitial matter of the crushed ganister, and this matter, together with the added lime, facilitates the conversion of quartz into those higher-temperature modifications of silica (especially tridymite) on which the refractory character and strength of the ground-mass of a silica-brick mainly depends.

In considering the qualities to be desired in silica-rocks, it is important to distinguish between the coarse ganister-fragments that form the aggregate of a brick, and the finely-ground material that supplies the high proportion of silica also present in the ground-mass. In the finished brick, the aggregate is little altered, and its properties are closely connected with the structure of the original rock, but are uninfluenced by the additions of lime, etc., made before firing. In the ground-mass, on the other hand, the original structure of the rock is obliterated, and the main consideration would seem to be the chemical composition, which is dependent on that of the original rock and on the additions made. It will be seen that the properties of the rock used for the aggregate, are not necessarily those most useful for making the ground-mass.

In many British works the whole of the crushed ganister, after passing a screen, is used in the brick, and the aggregate and ground-mass are not separately graded. It is evident that no hard-and-fast distinction can here be drawn between the two; the exterior of the smaller quartz-grains is attacked and contributes to the ground-mass while the interior remains unaltered; nevertheless, the greater part of the ganister is represented by the larger fragments, so that the burned brick may conveniently be described as an aggregate of ganister imbedded in a ground-mass containing numerous quartz-grains. In France much attention has been given to the grading of the material, and 'impalpable' quartz from ball-mills has been used in the ground-mass so as to accelerate the development of the tridymite network.

The Silica-Rock.

It is a well-established fact that the high-temperature stability of a silica-rock itself, as used in the aggregate, is diminished by an undue proportion of constituents other than silica, such as felspar, kaolin, etc. A rock, therefore, with small, closely-packed grains and a small amount of interstitial matter is likely to produce a more stable brick than a coarser-textured rock of similar composition when burned under the same temperature-time conditions. It is easy to understand, from these considerations alone, why the Sheffield type of ganisters has proved so eminently suitable for use as the aggregate in the manufacture of silica-bricks.

It may be accepted as proved that rocks of the Sheffield type are more easily converted into sound silica-bricks of required refractory character and stability than any other quartzites and sandstones, but it does not follow that rocks differing from this

type in both texture and composition will not, under special treatment, furnish bricks of equal merit. In fact, moderately coarse-textured and pure quartzites, such as those of the Medina Formation, of which probably 85 per cent. of the American bricks are made, are manufactured into bricks of high quality. It must, however, be borne in mind that it is the practice to burn the bricks more completely in the United States than is customary in Britain. Similar remarks apply to Germany, where quartzites that differ considerably from our ganister type are used almost exclusively. In Britain the diversity of rocks used has given rise to a series of special treatments and much empirical handling of the raw material, especially in such matters as the grinding, amount of added bonding matter, and the temperature and duration of burning. There are, however, certain principles which may be applied to all rocks alike and which may be stated in general terms as follows:

The coarser the texture of a pure silica-rock, the smaller, within limits, should be the size of the rock-fragments produced by the crushing. The purer the silica-rock used in the ground-mass, the greater must be the proportion of added bonding material.

The purer the silica-rock used in the ground-mass, and the coarser the grinding, the longer must be the time of burning for an equal degree of conversion, and, conversely, the finer the quartz and the more evenly distributed the impurities and the added bonding material, the more rapidly will the required changes take place on heating.

The Bond.

To all silica-rocks in their crushed state or during the process of grinding, some foreign matter is added to form a bond on burning. In the majority of cases, this takes the form of milk of lime, although other materials have been used, either alone or with a proportionately reduced amount of lime. Aluminous compounds, in the form of clay, ferric oxide, slaked calcined magnesian limestone, and a number of artificial substances such as calcium chloride, aluminium sulphate, and colloidal silica, have been tried, with more or less success, but for general purposes lime seems to be satisfactory, especially when the silica-rock already contains a moderate amount of alumina and traces of other oxides.

The percentage of lime in a good silica-brick varies considerably according to the type of silica-rock used and the degree to which the crushing of the rock has been carried out, *i.e.*, the proportion of ground-mass in the brick. In the case of bricks made from the American quartzites, and other somewhat coarse-textured but pure quartzites, the percentage varies from 2 to 3, generally being about 2. The first effect of an increase is to render the brick more friable, while a further increase not only emphasises the friability, but progressively lowers the softening-point. In the case of our Coal-Measure ganisters, in which the impurity is greater and more evenly distributed, the quantity of added lime seldom reaches 2 per cent., while for quartzitic rocks that contain more alumina, ferric oxide, magnesia, and alkalies,

1 to 1·5 per cent. is probably about the right proportion. With rocks containing a higher percentage of impurity, the addition of only 1 per cent. of lime often makes a brick which is too friable for general use, while as much as 1·5 per cent. unduly reduces its refractory character. It would appear, therefore, that the percentage of added lime may vary within such limits as from 1 to 3. Efficient mixing of the lime with the rock powder is all-important, for the bonding material must be equally disseminated throughout the whole mass in order to produce a ground-mass of equal stability and refractoriness throughout, with a maximum yield of tridymite. Further, it is obvious, that by thorough mixing and fine grinding, the proportion of added bonding material may be reduced and refractoriness thereby increased.

The effect of the added lime in aiding the conversion of quartz into the higher-temperature forms of silica has been proved experimentally by Seaver, who finds that in a lime-quartzite brick the amount of conversion is 77·35 per cent. as compared with 48·95 per cent. in the quartzite itself under the same temperature-time conditions.

If pure quartz and calcium oxide are heated together, they combine to form various calcium silicates of which the stable meta-silicate $CaO.SiO_2$, melting at 1,540° C., and the less stable silicate $3CaO.2SiO_2$ are those with which we are probably most concerned. The reaction takes place freely with pure components between 1,400° C. and 1,500° C., when the meta-silicate is formed, and this compound is capable, in the presence of excess of silica, of forming an eutectic mixture which contains 37 per cent. CaO and which will remain liquid to as low a temperature as 1,436° C. It will be obvious, however, that the melting-temperatures of these pure compounds and even of the eutectic, are all well above those at which bonding occurs or, at any rate, commences in the burning of a silica-brick, and therefore the initiation of the process must be attributed to the presence of some other substance contained in the rock itself.

We have, therefore, to consider the effect of the presence of other bonding-materials beside lime. That usually present is alumina, which is generally derived from the rock used for making the ground-mass, but is occasionally added when required.

Inspection of the brick-analyses quoted on p. 55 will show that, in almost every case, the percentage of alumina approaches, but is somewhat lower than, that of lime. The data for the system CaO-Al_2O_3-SiO_2 are available (G. A. Rankin and F. E. Wright, *Amer. Jour. of Sci.*, vol. xxxix, p. 40), and it may be of interest to trace for a moment the behaviour to be expected from a finely-ground brick made of pure materials. The diagram for the ternary system, as regards mixtures rich in silica, is reproduced in Fig. 2.

If lime and silica alone are present, combination may take place slowly on prolonged heating at low temperature—as indeed happens in certain cements below the melting-point—but it is not until the eutectic temperature, 1,436° C., is reached that a liquid will make its appearance. In dealing with absolutely pure

materials delay is sometimes met with in the combination of the two oxides which form the compound CaO. SiO_2, but in practice, on prolonged heating and with slight amounts of other impurities present, it is likely that equilibrium will be attained, as is evidently the case in ordinary silica-bricks. The eutectic contains the whole of the lime, together with sufficient silica to form 63 per cent. of the melt. If we assume that the ideal brick contains 3 per cent. of CaO, the total percentage of eutectic melt at 1,436° C. will be 8·1. The rest of the silica remains in the solid state but undergoes regrowth to form tridymite; this is accompanied by a slight disturbance in the composition of the melt due to the greater solubility of quartz. In a pure lime-silica brick, then, the proportion of melt is small and the temperature at which it is formed lies very close to that at which the bricks are burned.

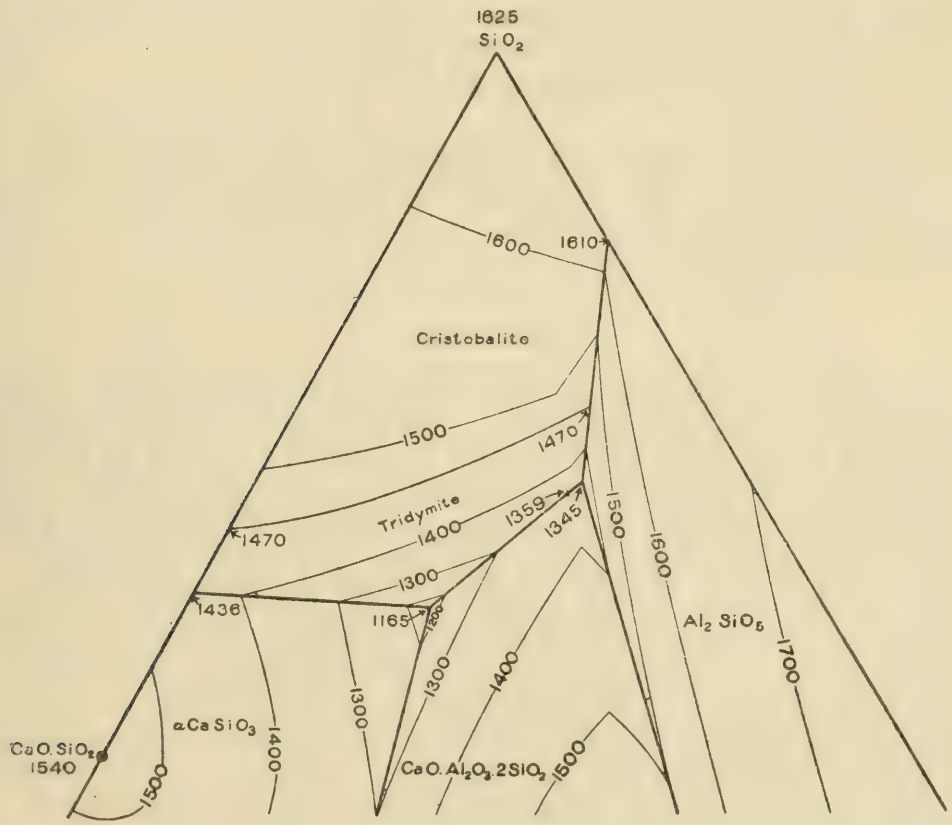


FIG. 2.—Portion of the Ternary Diagram for the System CaO—Al_2O_3—SiO_2. The heavy lines represent the compositions of the binary eutectics, and the enclosed areas indicate the composition of the melts that are in equilibrium with the mineral named in each area at the temperatures shown by the contour-lines.

If alumina and silica alone are used in the brick, the melting-point of the eutectic is even higher, namely, 1,610° C., and no melt at all will be formed at normal burning temperatures. It is, therefore, the behaviour of the ternary mixtures that has special interest in the manufacture of silica-bricks. When alumina is added to the lime-brick, or when lime is added to the alumina-brick, the melting-point of the eutectic is lowered, and the composition of the eutectic mixture varies along the strong lines

shown in the adjoining diagram. The maximum depression is considerable, for the ternary eutectic, which has the composition CaO 23·25, Al_2O_3 14·75, SiO_2 63 per cent., melts at 1,165° C. Thus by the addition of alumina to a lime-brick, the eutectic temperature can be lowered by no less than 266° C. Moreover, the percentage of silica in the eutectic is practically unaltered. The last is a very important matter, for the softening-point of the brick at the highest temperatures is dependent upon the amount of impurities present, the total allowable being probably not more than 4 per cent. At 1,165° the percentage of melt (eutectic) present in a 97 per cent. silica-brick would already be about 8, and as the temperature rose the proportion would increase. At 1,450°, according to the diagram, the melt would contain 71 per cent. of silica, and the proportion of melt in the brick would be a little over 10 per cent. This increase in the melt is again an advantage, in that it will accelerate the conversion of the silica ground-mass to tridymite, for this depends on solution of the quartz in the liquid present.

It would seem then that the ideal brick might contain, say, SiO_2 97, Al_2O_3 1·2, CaO 1·8 per cent. In practice the presence of impurities will modify this composition, and it must not be regarded as in any way essential, but the example may serve to illustrate the considerations that underlie the selection of a suitable bond for silica-bricks.

Burning.

The effect of burning a raw silica-brick is two-fold: firstly, to produce a siliceous melt that will permeate the ground-mass and act as a cement, and, secondly, to convert as much as possible of the quartz in the ground-mass into a felted aggregate of tridymite-crystals, whereby the greatest permanent expansion is given to the brick and the refractory character is greatly increased.

The production of the siliceous bond has already been discussed, but the conversion of quartz, on which so much has been written lately, also leaves much room for experiment and research.

A study of thin sections of burned bricks and also of bricks that have had prolonged use in a furnace, shows that the conversion of quartz begins mainly at the outer surfaces of the quartz-grains, those surfaces being either the original boundaries of the grains or the result of fracturing by grinding or thermal expansion. Further, we see that after a brick has been burnt at a temperature well above that at which quartz is supposed to change its crystalline state, and even after its long-continued use in a furnace, much unconverted quartz still exists in the cores of the grains. It would appear that the conversion takes place more readily in quartz that is in contact with the siliceous melt, than in that which is free from impurity of any kind. It may be taken as established that after its initiation the progress of conversion rapidly diminishes in velocity, so that it is only with a steady rise in the temperature of the kiln towards the melting-point of quartz that a higher degree of conversion can be obtained.

For a successful brick it is desirable that the permanent expansion attendant on the conversion, which theoretically exceeds

13 per cent., should be as far as possible accomplished in the kiln, and that no undue further expansion should take place in the furnace. By this we do not mean that all the quartz must be converted, but that the brick should be brought in the kiln to such a state that further conversion may be so slow and the attendant permanent expansion so small as to cause no inconvenience. Viewed solely from the aspect of refractory character and permanent expansion, it is of course desirable that as much as possible of the original quartz of the raw brick should be converted, but practically the main consideration is the amount that can be converted in a reasonable time with a reasonable consumption of fuel and without damage to other properties essential to the brick. According to Seaver, a lime-silica brick burned for forty hours at 1,540° C. had 77·35 per cent. of its quartz converted; a second burning of like duration and temperature raised the percentage to 82·87, while a third raised it only to 83·98. From this we may deduce that the maximum change takes place in the first burning, and that a state is reached in which, although unconverted quartz is present, its rate of conversion and the consequent expansion are so slow and small as to be readily dealt with. Similar experiments carried out by Seaver on the silica-rock showed that a much lower degree of conversion was reached on the first burning, only 48·95 per cent., while the second gave 68·62, showing how much more slowly and more steadily the change takes place without the addition of material such as lime, which, with the impurities already present, is capable of forming at a reasonably low temperature a sufficient volume of melt to permeate the brick. Further, from the above, it will be seen that the presence of large grains or fragments of homogeneous quartz will delay and lengthen out the process of conversion, and thus correspondingly lengthen the time during which the brick will be subject to permanent expansion. If, on the other hand, the ground-mass is made with finely-ground silica, the chief expansion will occur rapidly on firing and will be succeeded only by the slow conversion of the ganister-fragments.

It is commonly stated that British bricks are not sufficiently burnt. There is sometimes truth in the criticism, but as the temperature and time required for burning must of necessity vary according to the method of manufacture of the 'green' brick and the purpose for which the brick is required, no definite rules can be formulated. If permanent expansion in furnaces is to be avoided, a dense brick will certainly have to be fired more completely than one of open texture, for in a porous brick some of the expansion consequent on reheating may be taken up by the interstitial spaces. Further, a brick with much siliceous meal will convert more rapidly and more completely than one in which the quartz-fragments are larger. Improvement may therefore be effected by judicious choice of texture rather than by increasing the temperature and time of burning.

In the important stage of the initial burning the results are influenced by the rate at which the temperature of the kiln is raised. It is an advantage to heat slowly up to 800° C., at which temperature the quartz-conversion itself may first begin; and

again, above this, slow increase may be expected to ensure the more complete and economical conversion of quartz and the production of the stronger brick. Moreover, the slowness favours the formation of larger crystals of tridymite in the matrix, and these, by their angularity and interlacing, add to the stability of the brick. This effect is well exemplified by the used brick, in which the crystals of tridymite attain relatively large dimensions (*see* Figs. 4 and 5, Pl. VII).

That the conversion should be started and carried out at as low a temperature as possible is desirable. Rapid rises or falls of temperature tend to produce an undue amount of glass and to set up strains or actual planes of weakness in the brick.

An outstanding feature of the alteration of ganister-fragments (*see* p. 59) is the failure of the interstitial flux to produce tridymite; this might, it is true, be attributed to the chemical composition of the flux, but it must be admitted that its chemical difference from the ground-mass is hardly sufficient in itself to explain the total absence of tridymite, and that some further explanation must be sought.

The ganisters are characterised by the predominance of Fe_2O_3 and Al_2O_3 over the other impurities; this in all probability raises the eutectic point and so, when the ganister is fired, the low-temperature stage may be passed before the melt appears. At the full burning-temperature, cristobalite is nearly as stable as tridymite, and appears very readily; it seems possible, then, that when cristobalite is once present the degree of supersaturation attainable is insufficient for the production of tridymite, which, therefore, does not appear in the ganister.

Whether the following remarks can be held to throw light on this question or not, it is certain that the application of the principle deserves serious consideration in connexion with the structure of silica-bricks.

General considerations.—It is now well recognised that for every substance crystallising from solution there exists a certain interval of supersaturation within which no crystals will appear, even when it is held at a temperature below the true freezing-point, unless crystalline nuclei are already present; this is termed the metastable range, and at ordinary temperatures extends for, it may be, 20 degrees below the freezing-point but has a characteristic value for each case. At high temperatures the range may average 50 degrees and greatly influences the course of crystallisation. The curve defining the limit of the metastable state of the solution lies below and roughly parallel to the ordinary solubility curve; it is termed the supersolubility curve, and beyond it the solution is said to be labile and spontaneous crystallisation can occur.

If it is assumed that cristobalite and tridymite exhibit the usual phenomena connected with supersaturation, their behaviour will be represented by such a diagram as that shown in Fig. 3. The heavy lines are the solubility curves of the two forms in contact with a melt. Below each curve has been drawn the supersolubility curve at an interval of about 50°. The behaviour

to be expected from a melt originally free from nuclei when held without agitation at temperatures within the respective areas will be as follows:—

1. Unshaded area.—No fresh nuclei will appear and the melt remains fluid, but is supersaturated with respect to one or both forms.

2. Oblique shading.—The melt is metastable with respect to tridymite, or even fully stable at the highest temperature, but is labile for cristobalite, which will therefore appear. As soon as crystals have formed the melt assumes the composition indicated by the true solubility curve for cristobalite. This area may well extend to a temperature 100° or more below the true transition point (1,470°). The theoretical limit is indicated by the intersection of the supersolubility curves.

3. Horizontal shading.—Cristobalite is metastable, tridymite is labile, and will therefore crystallise; the melt will then assume the composition indicated by the solubility curve for tridymite.

4. Vertical shading.—Both forms are labile, but there is strong reason to anticipate that cristobalite will appear first (*see* p. 58). If this occurs the melt assumes the composition indicated by the cristobalite solubility curve, which is unstable at temperatures below 1,470° C. but, for part of its course at least, will lie within the metastable range for tridymite, as shown in the diagram. If this is the case tridymite need not necessarily appear for a long period when once the other form has crystallised.

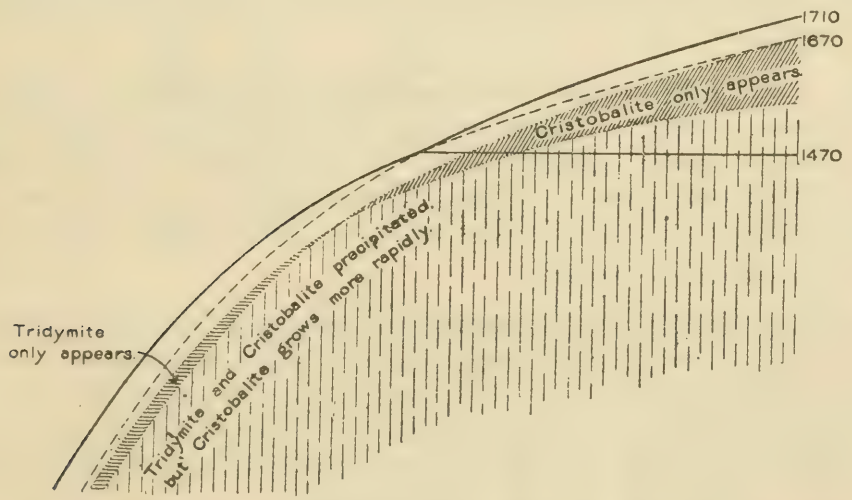


FIG. 3.—Diagram to illustrate the conditions that govern the crystallisation of silica from undisturbed melts in the absence of nuclei.

It will be seen that in each case, when once cristobalite has appeared, the subsequent formation of tridymite nuclei becomes improbable. This is especially true for temperatures just below 1,470°, and the effect will be that unless a sufficient supply of tridymite nuclei is already present, the transition to the normal

felted structure may be replaced by the formation of a granular cristobalite structure that will present the appearance of having been overheated, and will no doubt materially affect the properties of the brick.

The silica-bricks may be divided into two classes, those in which the silica-rock fragments are of variable but visible dimensions, and those which present a more or less even texture and are devoid of obvious rock-fragments.

In the first class belong the majority, including the well-known Dinas and Sheffield types, while under the latter heading are included the less common sand-bricks and bricks made from silica-rocks reduced to a relatively fine state of division.

Practically all British silica-bricks, in their fine-textured portions, are of a pale-yellow to palest buff colour, but the silica-rock fragments, except for a marginal coloration, retain their original whiteness, or become white on burning. Such also is the character of most of the bricks made in the United States from the Medina and other quartzites. In the coarse-textured bricks, the size and proportion of silica-rock fragments vary in accordance with no special rule and appear to be largely a matter of custom and expediency.

Chemical Analysis.

Chemically the analyses of the burned brick are just what might be expected from the analyses of the rock used and the composition of the added bonding material. Typical analyses are given on p. 55.

These analyses merely show a higher percentage of lime than the silica-rock, and a relative reduction in the percentages of all other constituents; silica-bricks of best quality rarely contain more than 2 per cent. of lime. The influence of chemical composition upon the properties of the brick has already been discussed (pp. 47 *et seq.*).

In recent work on the strength of bricks it has been suggested that the total weight of basic oxides, when converted into sulphates after volatilisation of the silica, might serve as a measure of the quality of the brick. The strength of the brick will depend upon the proportion of melt formed, and this can only be known when the curve of depression of freezing point for the fluxes in question has been ascertained. At present there is little direct information on this question, but it is certain that to produce the same depression quite different weights of the various oxides will be necessary, and thus some oxides will be more damaging than others. At present, then, it would appear that a complete analysis is greatly to be preferred for the purpose of estimating the refractory value of a brick.

	I.	II.	III.	IV.	V.	VI.	VII.
SiO_2 ...	94·90	96·175	96·88	96·90	95·74	95·30	98·31
Al_2O_3 ...	1·52	1·030	·80	·45	1·06	1·52	·72
Fe_2O_3 ...	1·34	·884	·60	1·12	·54	·52	·18
CaO ...	1·90	1·843	1·45	·90	1·32	1·76	·22
MgO ...	trace	trace	·02	trace	·28	·19	—
K_2O ...	} ·55	—	·25	·39	·87	·64	·14
Na_2O ...	}						
TiO_2 ...	—	—	—	—	—	—	—
H_2O ...	—	—	—	—	—	—	·35
Loss on ignition.	—	—	—	—	—	—	—
Total ...	100·21	99·932	100·00	99·76	99·81	99·93	99·92

I.—Representative Silica Brick, Yorkshire. Analysis communicated by D. Colville & Sons, Ltd., Motherwell.

II. & III.—Burnt Ganister Bricks. The West Witton Ganister Firebrick Co., Ltd., Hunwick, Willington, S.O., Co. Durham.

IV.—Representative Silica Brick from Co. Durham. Analysis communicated by D. Colville & Sons, Ltd., Motherwell.

V.—Representative Silica Brick, N. Wales. Analysis communicated by D. Colville & Sons, Ltd., Motherwell.

VI.—J. B. Jenkins' best Silica Brick. Analyst not recorded.

VII.—Vale of Neath Silica Firebrick, &c. Co., Ltd. Anal. Dr. Percy.

	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.
SiO_2 ...	96·73	94·80	97·32	94·90	96·20	96·15	95·60
Al_2O_3 ...	1·39	2·10	1·04	1·63	·82	1·79	1·02
Fe_2O_3 ...	·48	·57	·43	1·07	·84	·73	·98
CaO ...	·20	1·80	·95	2·14	1·20	1·06	1·30
MgO ...	—	·40	·04	·27	—	—	trace
K_2O ...	} ·19	·29	·04	—	—	—	1·12
Na_2O ...	}						
TiO_2 ...	—	—	·13	—	—	—	—
H_2O ...	·50	·40	—	—	—	—	—
Loss on ignition.	—	—	—	—	—	·25	—
Total ...	99·49	100·36	99·95	100·01	99·06	99·98	100·02

VIII.—Vale of Neath Silica Firebrick, &c., Co., Ltd. Analysis by Dr. Percy.

IX.—Penwyllt Dinas Silica Brick Co. Analysis by Pattinson & Stead, Middlesbrough.

X.—N. B. Allen & Co., Hirwaun. Analysis by J. & H. S. Pattensen, Newcastle-on-Tyne.

XI.—N. B. Allen & Co., Hirwaun (new analysis). Analysis by J. & H. S. Pattensen, Newcastle-on-Tyne.

XII.—H. & H. E. Smart, Kidwelly. Analysis by Wm. Morgan, Swansea.

XIII.—Stephens & Co., Kidwelly. Analysis by J. S. Merry & Co., Swansea.

XIV.—Representative Silica Brick, S. Wales. Analysis communicated by D. Colville & Sons, Ltd.

Density.

That the density of a silica-brick is influenced by the time and temperature of burning is well known. The conversion of the quartz is accompanied by a notable increase in volume, and this is fairly well indicated by the density of the crushed material, provided that the silica content is high. In order to determine the degree of conversion in this way, it is essential to break up the numerous fine cavities, and grinding must therefore be carried as far as possible. The determination gives a useful means of comparing the quality of bricks made by the same methods, but the differences between different makes of good bricks are so great that this property cannot serve as a general test of their value.

The volume-density, that is, the weight per unit volume of the dry brick, is easily determined and is a useful constant. Taken with the density of the crushed material it affords a means of calculating the porosity, while in itself it is a measure of the amount of silica put into the structure. The weight per thousand for different makes of a standard shape is very variable, and must in itself affect the durability of the lining.

The density of the crushed brick varies from that of nearly pure tridymite (or cristobalite), 2·28, up to a value approaching that of quartz, 2·66. The volume-density may vary between 1·50 and 1·88; it is usually about 1·67, in grams per cubic centimetre.

The porosity of the burned brick is mainly determined by that of the raw material, and depends on grading, etc.; it usually lies between 20 and 30 per cent. and is not greatly altered by repeated burning in the case of light bricks, but increases somewhat for heavy bricks.

Strength.

The strength of a silica-brick has been investigated by several observers and values have been obtained for the crushing-strength of different parts of the bricks, such as sides, edges, and ends; and also for the crushing-strength and modulus of rupture as influenced by repeated burning.

The crushing-strength varies from 1,000 lbs. to 4,500 lbs. per square inch, and is increased slightly by continued or repeated burning, but the modulus of rupture shows a striking increase with repeated burning, and, according to figures given by Seaver, rises from 624 lbs. per square inch on a brick that has been burned once, to 1,001 lbs. for the same brick burned three times. It must be borne in mind, however, that the crushing-strength of a brick is no indication of its refractory character.

According to Le Chatelier the crushing-strength diminishes steadily with rising temperature; bricks that gave at 15° C. 2,418 lbs. per square inch showed at 1,050° C. 1,707 lbs., at 1,460° C. 711 lbs., and at 1,600° C. 427 lbs.

Expansion.

The permanent linear expansion of a silica-brick on burning is usually from 1·6 to 2·1 per cent. This is due to both mineralogical and textural changes, and probably as much to the increased porosity and other structural changes as to the much-discussed

volume-changes produced by the conversion of quartz. In support of the above statement it is asserted that most of the expansion occurs below the temperature of 600° C. The fact remains, however, that for certain purposes most of the permanent expansion of a brick can, and must, be effected during the process of burning, so as to diminish as far as possible the volume-changes in the fabric of the furnace.

Allotropic Modifications of Silica.

Before describing the micro-structure of silica-bricks, it may be well to give an account of the three modifications of silica that are met with in silica refractories.

Quartz.

Density 2·66. Characterised in thin sections by its relatively high refractive index (1·544 to 1·553) and bi-refringence (0·009). In silica-bricks, generally devoid of crystalline boundaries. During firing, irregular fractures develop in the grains. When heated to about 575° C., quartz undergoes a reversible transition to a form (β-quartz) of slightly different symmetry, the change being accompanied by a sudden expansion and a corresponding change in specific volume from 0·390 to 0·397. β-quartz has apparently a very low coefficient of heat-expansion. When a temperature of about 1,200° C. is attained β-quartz begins to transform slowly to cristobalite. The velocity of this change increases with the temperature, so that it is difficult to realise the melting-point of β-quartz, but this has been estimated to be in the neighbourhood of 1,600°C. The fusion at this temperature is accompanied by a rapid transition to cristobalite. In a recent experiment clear quartz, heated for 100 hours at from 1,300° C. to 1,400° C., was almost completely converted into cristobalite with a few grains of tridymite.

Quartz is essentially a low-temperature mineral, and neither grows nor is deposited in silica-bricks, during either their manufacture or use.

Tridymite.

At temperatures above 870° C. quartz is unstable, but in the absence of a flux the transition is suspended as described above, although between the temperatures of 870° C. and 1,470° C., tridymite, and above 1,470° C. cristobalite are the respective stable forms of silica. In the presence of fused matter conversion usually takes place readily, the quartz being dissolved while tridymite crystals grow in the melt, but the speed of conversion depends on the chemical nature of the melt.

Tridymite builds platy crystals, with hexagonal outline and lath-shaped cross-section; it has a highly characteristic mode of twinning, and in bricks that have been subjected to prolonged heating within the stability range forms conspicuous arrow-head twins, of which the size increases with the period of heating.

Like quartz, tridymite can be superheated to its melting point at about 1,670° C., 200° C. above its transition point to cristobalite. On cooling, crystals of tridymite do not revert to quartz

on passing the temperature of 870° C., except on continued heating especially in the presence of a flux, but at temperatures of 163° C. and 117° C. they pass by reversible transformations, accompanied by small volume-changes and characteristic alterations in internal structure, into forms of lower crystalline symmetry, termed β -, and α-tridymite, β_2-tridymite being the highest temperature form.

α -tridymite (the lowest temperature form), has a density of 2·28, refractive indices 1·469 to 1·473, and bi-refringence 0·004.

Cristobalite.

Cristobalite is the stable form of silica between 1,470° C. and its melting-point of 1,710° C., and crystallises in the cubic system. On rapid cooling, it does not revert either to tridymite or to quartz, but undergoes a reversible though ill-defined transition in the neighbourhood of 250° C., when it becomes anisotropic and undergoes a very considerable diminution of volume, the specific volume changing from 0·451 to 0·430. The low-temperature form, known as α - cristobalite, has a density of 2·34, a mean refractive index of 1·485 and a low bi-refringence. The crystals as seen in micro-sections are always fractured, owing to the volume-changes on conversion, and between crossed nicols exhibit a characteristic chequered pattern, owing to the fact that they are composed of a mozaic of α - cristobalite, of which the orientation has a definite relation to the original cubic symmetry of the β-cristobalite crystal.

Various methods have been employed to distinguish between the varieties of silica described above and to estimate their proportion in silica-bricks.

Apart from the crystalline form which is not always observable, the character of a grain can be readily determined by immersion in a liquid of which the index of refraction is equal to the mean index of tridymite for yellow light. This method has been described in the Journal of the Iron and Steel Institute for 1918, No. II, p. 104.

In the formation of the silica minerals, many examples of suspended or retarded transformation are encountered.

In considering the slow transition from a meta-stable to a stable solid phase, it must be borne in mind that the appearance of the new phase is conditional on the formation of crystalline nuclei of that phase. The probability of the formation of such nuclei will depend upon the extent to which the system departs from equilibrium and also upon the temperature-conditions and viscosity. Further, it appears to be an essential property which varies widely for different substances. In considering the conversion of quartz, many apparently contradictory results seem possible of correlation if we recognise that under the same conditions the probability of the appearance of a nucleus is considerably greater for cristobalite than for tridymite and, similarly, that the rate of crystal-growth of cristobalite, when once formed, is greater than that of tridymite. This relative rapidity of the crystal-growth is reflected in the habit of freely-growing crystals of cristobalite, which are almost always

dendritic or skeletal. The fact that, in many instances, an unstable phase appears in preference to a stable phase, has long been recognised and is known as Ostwald's Principle. This may be illustrated by the following examples:—

(*a*) Pure quartz, subjected to dry heat between the temperatures of 1,360° C. and 1,400° C. was mainly converted into cristobalite, but this was accompanied by the formation of a few nuclei of tridymite.

(*b*) Siliceous melts, on rapid cooling, at temperatures below 1,470° C., yield numerous cristobalite crystals even when nuclei of tridymite are present and when tridymite is the stable phase. There can be no doubt that on prolonged heating at such temperatures the cristobalite would pass slowly over into tridymite.

(*c*) Quartz-glass, and other glasses rich in silica, heated below 1,470° C., first devitrify with the formation of cristobalite.

Micro-structural Changes in Silica-bricks on Burning.

In discussing the microscopic characters of silica-bricks, it will be well to consider separately the alterations and final structure produced by burning (*a*) in the ganister-fragments and (*b*) in the ground-mass.

(*a*) *Ganister-fragments.*—Compound ganister-fragments, that is to say, fragments composed of a number of homogeneous quartz-grains naturally cemented together, show but little sign of marginal absorption by the ground-mass, but exhibit a series of highly characteristic internal changes. The most striking feature is the development of numerous irregular cracks throughout the component quartz-grains. The interstitial matter of the ganister, originally present as barely visible cementing films, attacks the quartz, with the formation of a highly siliceous melt that surrounds the grains, penetrating along the cracks and separating the component fragments of the broken crystals. The quantity of interstitial melt so formed is dependent on the amount and nature of the impurity present and on the temperature. It reaches a limit which is not altered by prolonged heating. The melt solidifies to an isotropic glass which is normally colourless but is tinted with yellow if iron is present in the ganister, and which occasionally shows signs of devitrification. The refractive index is considerably lower than that of the quartz which it envelopes.

Normally, on prolonged heating at the usual burning-temperatures in the presence of a flux, quartz is transformed into tridymite, but an examination of the ganister-fragments in numerous British bricks has in no case revealed the presence of tridymite. According to American authorities, much of the quartz of the silica-rock fragments is converted into cristobalite, as in the dry conversion of quartz. This change can be observed in the British bricks, but does not occur to the same extent, and it must therefore be presumed that, in this country, the general practice is to burn the bricks either for a shorter time or at a lower temperature.

The quartz-fragments and interstitial glass of a typical ganister-fragment from a British brick that has been used in a furnace are illustrated in Fig. 4*a*, p. 67. It will be seen that the lines of interstitial glass are separated from the residual quartz-fragments

by a clear material of low refractive index. This material can often be readily distinguished from the glass that marks the original position of the crack. As the time of firing is prolonged it gradually eats into and finally replaces the quartz. That it is a conversion-form of silica seems clear, but since it is in most cases sensibly isotropic there is a doubt whether it is quartz-glass or a cryptocrystalline form of cristobalite. The stability under prolonged heating points strongly to the latter conclusion, which is generally adopted and seems to be confirmed by refractive index determinations.

The extent to which this conversion occurs is an important feature of the burnt brick. In British bricks the proportion of quartz altered is not often sufficient to have a direct effect upon the physical properties, but in American bricks the conversion of the ganister is greater and may exceed 50 per cent.

Whatever theoretical views may be held as to the importance of securing a high degree of conversion in the brick as a whole, it must be remembered that in actual practice, based on many years of experience, most of the best British bricks show little or no conversion of the ganister-fragments, and that the ganisters most liked for making the aggregate are those in which conversion, so far from being easy, is rendered difficult by the chemical nature and deficiency in quantity of the interstitial impurities.

(*b*) *Ground-mass.*—In the ground-mass, in which the quartz is in a fine state of sub-division, and in which is concentrated the added bonding material, the final structure is a felted aggregate of minute tridymite crystals embedded in an isotropic glass. Where large quartz-grains are present, especially as in the sand-bricks, fragments of unaltered quartz remain scattered throughout the mass. Here again, in the British bricks, cristobalite is apparently absent, whether the temperature of burning has or has not exceeded the transition point of 1,470° C. While the brick is maintained at the burning-temperature, the melt becomes saturated with quartz derived from the solution of minute fragments and of the marginal portions of the larger grains of this mineral; it is then supersaturated with respect to tridymite, crystals of which, therefore, grow to form an interlacing mass of considerable rigidity. When the brick cools the crystals undergo a small additional growth, due to the separation of silica from the interstitial melt. The residue of the melt solidifies as a glass which, in the average brick, shows practically no signs of devitrification. The coarseness of the tridymite-structure increases as the burning is prolonged, the larger crystals growing at the expense of the smaller. The solution of quartz also continues, but with the disappearance of the small grains and the consequent diminution of the effective area of quartz, the rate of conversion is greatly reduced.

In comparing different bricks it is important to note the size of the tridymite-crystals, the proportion of tridymite to glass, and the extent to which the smaller quartz-fragments have been assimilated. In well-fired bricks the fine quartz has disappeared, leaving only larger and somewhat rounded grains, which are imbedded in a uniform felted aggregate of tridymite-crystals, the

characteristic form of which can be distinguished with a quarter-inch objective. If the brick is less completely converted, the smaller quartz-grains remain, and the tridymite is barely, or not at all, distinguishable. In an extreme case, where, apparently, little fine quartz had been used, the glass had remained so rich in lime as to deposit a crystalline, highly birefringent silicate, which served as a cement to an aggregate of unaltered quartz.

Microsections.

Photographs of thin sections of four typical silica-bricks are shown in Plate IV. The sections are seen in transmitted light between crossed nicols, and in order to reveal the structure of the isotropic portions the prisms have been set at a slight angle from the extinction-position, so that the background appears half-tone. Unaltered quartz in the ganister or ground-mass exhibits a range of tones depending on the orientation of the grains, but is for the most part brighter than the background. The transparent isotropic alteration-product (cristobalite) has the same tint as the background, while the turbid ground-mass appears black. The wide variation in the degree of conversion of the quartz will be realised from a comparison of the following descriptions.

Plate IV.

Fig. 1. *American Silica-brick.* A very well-burned brick.

Ganister.—The quartz-grains have been largely converted, but the outline of the grains can still be distinguished, as also the boundary of the fragment which occupies the lower part of the field. A few grains contain unaltered quartz that is penetrated by numerous cracks along which conversion is in progress.

Ground-mass.—Very little unaltered quartz remains; the grains are outlined with turbid material, which under high magnification shows a well-developed tridymite-network that extends throughout the mass. No clastic quartz or small grains can be seen.

Fig. 2. *British Silica-brick, South Wales.* Well burned, but not so completely altered as the preceding.

Ganister.—Most quartz-grains show an unaltered core with numerous cracks.

Ground-mass.—Only the largest quartz-grains remain unconverted. Tridymite is clearly seen with the higher power.

Fig. 3. *French Silica-brick.* Made from very pure materials and free from iron staining. Conversion has probably been retarded on account of the purity of the constituents.

Ganister.—Nearly unaltered; the quartz is clear and free from cracks, with practically no conversion.

Ground-mass.—The large grains are unaltered, smaller clastic quartz is also visible, but tridymite is developed in the interstitial matter.

Fig. 4. *Sheffield Silica-brick.* Exhibits a large proportion of unaltered quartz, the ground-mass having been well packed with large grains.

Ganister.—The grains are somewhat cracked and conversion is beginning along the margins.

Ground-mass.—The large grains are unaltered except at the margins. Interstitial tridymite-network is well developed but is very small in amount in proportion to the quartz present.

CHAPTER VII.

Structural changes produced in Silica-Bricks during Service.

Most of the silica-bricks made in this country are employed for the construction of steel-furnaces, and the following description relates, except where otherwise stated, to bricks so used. A certain number are used for lining soaking pits and electric furnaces, but by far the greater part is consumed in the construction and repair of acid and basic open-hearth furnaces; in both of which (with minor exceptions) the whole of the structure exposed to the gases is built of silica-brick. The temperature of the flame itself has been estimated to be in the neighbourhood of 1,700° C. to 1,800° C., while the temperature attained on the interior surface of the furnace is generally believed to be about 1,600° C. to 1,650° C., but an accurate estimate is difficult on account of the strongly reflecting nature of the surface. Since these temperatures lie very close to the melting range of silica-brick it will be seen that a brick, maintained at the full heat of the furnace, would possess little or no rigidity even if it could be protected from the action of foreign matter carried by the gases. A most important part of furnace design is therefore the efficient cooling of the structure, so that the hot zone is restricted as far as possible to the inner surface of the brick-work, while the structural stresses are borne by portions of the brick which are generally far below the softening-point. With every precaution, however, the inner surface is slowly corroded by a constant fluxing-action, and no portion of the lining is permanent: The life of the structure at any part depends on the temperature and on the degree to which the bricks are exposed to the fluxing compounds borne by the furnace gases.

Probably the bricks which form the wall separating the air- and gas-ports are those which are subjected to the highest temperature. The wall is necessarily thick, it is exposed on three sides to the burnt gases leaving the furnace and has a correspondingly small cooling surface. It is not necessary to discuss the numerous devices that have been proposed for the extension of the life of the structure at this point, but it should be observed that here, rather than in the roof or walls, the strength of the brick at high temperatures becomes an essential factor in the durability of the furnace.

Beside the silica-bricks in the furnace-lining itself, a considerable quantity is used in the chequer work of the regenerators. The difficulties here centre mainly in the accumulation and corrosive action of foreign matter, for except in the uppermost courses the temperature is well below the softening-point, and bricks of inferior quality can be used. The service of the regenerators is normally determined by the choking of the

passages and does not depend on the refractory property of the bricks used. In the case of silica-bricks in the furnace-lining, so important is corrosion that refractory characters again play but a subordinate part.

CHANGES IN BRICKS WHEN HEATED IN THE ABSENCE OF FOREIGN MATTER.

The heat-alteration of a silica-brick at a moderate temperature represents simply the extension of changes initiated in the burning operation as already described. When the temperature exceeds 1,470° C., the tridymite ground-mass and the ganister-fragments ultimately become converted into a granular aggregate of cristobalite. In this condition the brick retains rigidity under moderate stresses. Thus, even the 'bank' of a steel furnace and the brickwork between the ports retain their shape. As the temperature increases above the transition-point, the fluid areas expand, owing to the solution of the cristobalite, until, at a temperature that depends on the amount of impurities present, the whole structure becomes fluid, and all rigidity is lost. The purer the brick, the higher is this temperature; but in no case can the structure remain rigid above 1,710° C., the melting-point of pure cristobalite.

Perhaps it will be well at this point to call attention to an apparent anomaly in the behaviour of silica-bricks, which is to a great degree the basis for the divergence of views between certain workers as to the real existence of the 1,470° C. transition-point.

It has been observed that bricks heated to temperatures above the transition-point exhibit, on cooling, the ordinary tridymite network. This structure is well seen in the bricks used as a protective tier in the kilns and which have been repeatedly burnt at the highest temperatures. Whether the normal kiln temperature is to be regarded as exceeding 1,470° C. or no, there can be no doubt that in laboratory tests the transition point has been exceeded without the development of cristobalite.

On reference to Fig. 3, p. 53, it will be seen that a melt saturated by being held in contact with tridymite above 1,470° C. is in a metastable condition with respect to cristobalite. In the absence of cristobalite nuclei precipitation of the truly stable phase may be indefinitely delayed. In the brick-kiln, therefore, the growth of the tridymite network can proceed even at temperatures above the transition-point, in those parts of the ground-mass that are free from cristobalite, and no sharp alteration in structure is to be expected if that temperature is exceeded.

CORROSION OF BRICKWORK BY FOREIGN MATTER DERIVED FROM THE CHARGE AND THE GASES.

In open-hearth steel-smelting furnaces, the foreign matter introduced as flue dust from the gas-producers is negligible in comparison with the amount of iron oxide that is emitted from the bath itself. As the temperature of the furnace rises after melting down, a rapidly increasing amount of pure iron oxide is

carried as a fine mist of liquid particles in the outgoing gases. This would seem to be an essential feature of the reaction; it is at a maximum during the 'boiling' period and diminishes towards the finish when the carbon is low. This oxide penetrates to every part of the gas-passages, and causes a rapid corrosion of the brickwork round the ports and in the uptakes where sharp changes in the direction of the gas cause the heavier particles to be projected against the walls. The greater part of it ultimately lodges in the chequer-chambers, where it gives rise to difficulties which, however, are not concerned with the refractory character of the brick there used. In an acid furnace the corroding agent is pure iron oxide and not slag or ore accidentally projected, but in the basic process a certain amount of lime is swept away in the gas and contributes to the corrosion, as will be seen below from the analyses of roof bricks. Locally, one of the most damaging actions is the casting of dolomite upon the banks in such a way that it falls above the part of the furnace built of magnesite bricks and comes into direct contact with the silica walls.

The lining of a furnace may be regarded as made up of a succession of zones—composed of fused matter, cristobalite, tridymite and then unaltered brick—which vary in thickness in different parts according to the efficiency of cooling and the degree of attack by foreign matter, but which are generally similar in character throughout the furnace. A roof-brick may be taken as illustrative of the alterations met with in other parts of the structure.

Analyses of used Roof Bricks.

Acid Furnace.

Zone.	SiO_2	Fe_2O_3	FeO	Al_2O_3	CaO	MgO	Mn_3O_4
A (cristobalite)	79·60	13·62	5·73	0·80	0·10	trace	0·29
B (tridymite)	74·76	19·03	4·47	1·10	0·30	trace	0·28
C (transition)	91·00	2·51	—	2·70	3·35	0·05	0·19
D (unaltered)	95·30	1·27	—	1·10	1·90	trace	0·20

E. Rengade, Anal.[1]

Zone.	SiO_2 [2]	Iron as Fe_2O_3	Al_2O_3	CaO	MgO	MnO
A (cristobalite)	84·62	14·1	0·60	0·35	0·03	0·30
B (tridymite)...	73·80	24·7	0·70	0·50	trace	0·30
C/D greenish ...	85·73	7·6	2·40	3·80	0·12	0·35
C/D yellow ...	95·50	1·0	1·60	1·80	0·10	trace
D slightly stained.	95·60	1·2	1·60	1·45	—	0·15

J. H. Whiteley, Anal.[3]

[1] E. Rengade, *Comptes Rendus*, vol. 166, 1918, p. 779.

[2] Silica by difference.

[3] J. H. Whiteley. Analyses made in order to locate more precisely the region of lime enrichment, and privately communicated for publication in the present Memoir.

Basic Furnace.

Zone.	SiO_2	Fe_2O_3	FeO	Al_2O_3	CaO	MgO	Mn_2O_3
A (cristobalite)	89·00	3·59	0·75	0·80	3·90	0·65	1·11
B (tridymite)...	88·80	4·39	0·50	0·70	3·85	0·72	1·00
C (transition)...	91·00	2·56	—	1·80	4·20	0·10	0·52
D (unaltered)...	97·30	0·48	—	0·70	1·15	trace	0·14

E. Rengade, Anal. [1].

Talbot Basic Furnace.([2])

Zone.	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Alk &c	S.G. p'wd'r	M.-P. °C.
A (cristobalite)	92·20	0·07	0·76	4·57	1·80	0·21	0·39	2·238	1,595
B_1 (tridymite)	89·17	0·19	1·12	5·64	3·00	0·47	0·41	2·393	1,580
B_2 (transition)	88·20	0·25	1·78	4·07	5·00	0·36	0·34	2·390	1,610
C (,,)	87·85	0·28	1·55	4·07	5·50	0·45	0·30	2·468	1,610
D (unaltered)	95·50	0·10	1·19	0·71	2·00	0·14	0·36	2·451	1,710

[1] E. Rengade. *Comptes Rendus*, vol. 166, 1918, p. 779.
[2] Analyses privately communicated by Dr. J. E. Stead for publication in the present Memoir. Zone A, P_2O_5=0·167.

The Roof Brick after use in a furnace.

The structure of a brick that has been in use in the roof of an acid furnace is shown in Plate V. Three main zones, termed A, B and C, have been described by Rengade. The approximate limits of these are indicated in the plate, but other divisions can be recognised, though their cause is not obvious. The brick differs from a pure brick similarly heated in that considerable quantities of iron oxide from the furnace have been absorbed, as is shown by the analyses given above. The internal surface, to which furnace gases have had access, is glazed and somewhat granular in texture. This represents the exterior of a thin layer of material that has been more or less completely fused, and it is by the flow of such a layer that corrosion of the brick takes place. Within this layer the proportion of solid cristobalite increases till a part of the brick is reached which has been at a temperature of 1,470° C. This is the limit of the cristobalite zone, which is from $\frac{1}{2}$ to $1\frac{1}{2}$ inches thick and has a white appearance due to numerous cracks. Beyond this limit the brick appears black, owing, on the one hand, to the increasing proportion of magnetite that has penetrated even the ganister-fragments, and, on the other hand, to the greater transparency and small size of the tridymite crystals. The tridymite zone is about 3 inches in thickness, and towards the cooler side its tint graduates into brown, owing to the falling off in the amount of iron, the local concentration of lime, and the presence of unstained fragments of ganister. The brown tint terminates at an abrupt boundary, but beyond this another zone, pale-brown in colour and characterised by the presence of much yellow glass, can sometimes be dis-

tinguished. Finally, a part of the brick is reached, in which there is no alteration except bleaching for a distance of about half-an-inch. The remaining external portion is usually stained to a light-brown tint.

Concerning the variations met with in different parts of the furnace, it will be sufficient to remark that where the brickwork has become thin in the roof or walls, the zones retain their relative dimensions, but are proportionately narrower. In the 'blocks' the brick is largely altered to cristobalite and has the structure of that zone. The form of the ganister-fragments can still be seen, but they have a fine porcellanous structure. In the ports and uptakes the rapid fluxing action tends to cut away the cristobalite zone, and the fluid layer is deeper and more highly charged with iron.

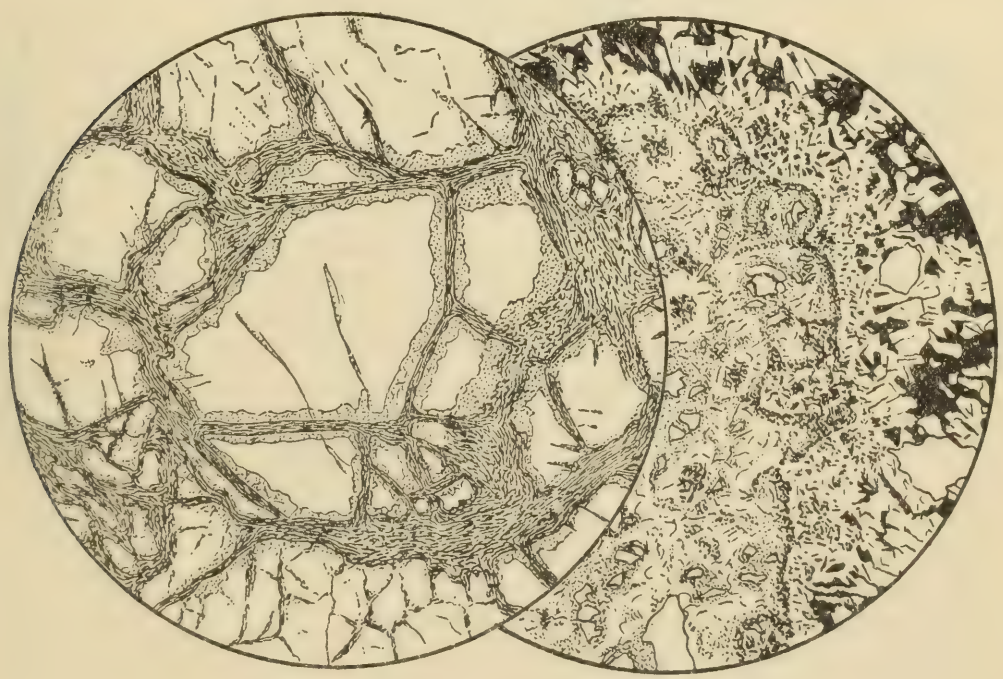
Micro-structure of the zones.

The Cristobalite Zone.—The fused layer is probably always charged with fragments of cristobalite, which, on cooling, serve as nuclei for crystallisation. The structure is thus a coarsely granular aggregate of cristobalite, commonly showing well-marked twin-structure (probably spinel-law), in the interstices of which are patches of originally fluid ferruginous slag. This slag contains much dendritic magnetite that has probably been formed in part by oxidation during the cooling of the brick in the furnace and is intergrown with tridymite, at times in a fayalite ground-mass. The same structure is found in the cristobalite zone itself, the main distinction being the existence of a greater amount of solid cristobalite at the high temperature (Plate VI, fig. 5). On account of the flatness of the freezing-point curve of cristobalite, the proportion of solid increases sharply with a slight fall in temperature, and, on cooling, the separation of most of the silica takes place at a temperature well above that at which the interstitial slag solidifies.

The Tridymite Zone.—The change of structure at the junction of this with the preceding zone is fairly well defined, the granular cristobalite giving place both in the ground-mass and in the ganister to a coarse-felted aggregate of tridymite with interstitial magnetite crystals. The ganister-fragments can be distinguished from the ground-mass by their finer grain, but are penetrated throughout by magnetite which occupies the interstices of the tridymite (Pl. VI, fig. 4). The predominant habit of the tridymite is an arrow-head twin. This is characteristic of those portions of silica refractories in which the tridymite has existed in the solid state at furnace-temperatures; the same substance when deposited from a slag on cooling has lath-shaped sections. The latter can be seen in places bordering the larger slag-areas and projecting into the magnetite, and indicate the extension of the fluid area at high temperatures.

Passage to the Unaltered Brick.—In the cooler portions of the tridymite zone the ganister-fragments are white and are not penetrated by iron.

The process of alteration of the ganister throws further light upon the difference between the ganister and ground-mass in the fired brick. The fragment, shown in Pl. VI, fig. 1, was situated about one inch within the limit of penetration of iron in the roof-brick and shows incipient penetration by iron. Scattered throughout the mass are pieces of the original quartz-grains. These are immediately surrounded by cristobalite, the conversion initiated in the burning having progressed in the furnace; between many grains can be seen narrow lines of glass. These structures are illustrated in greater detail by the drawings reproduced in Fig. 4. So far, the structure is that of a well-fired ganister. In places, however, the iron has already penetrated the rock, and can be seen as small grains of magnetite lying here and there in patches, no doubt along cracks and lines of weakness. Wherever the iron has entered, nuclei of tridymite have appeared, and the conversion to the normal felted structure has begun. The whole of the fragment has been heated to exactly the same extent, and it is therefore clear that the ' dry ' conversion of the quartz to cristobalite is dependent on the chemical nature of the interstitial matter, and is replaced, where the iron is present, by the normal change to tridymite.



a. *b.*

FIG. 4.—Used Silica-bricks; Microsections.

a.—Partly altered ganister fragment in used roof brick showing fractured quartz-grains separated by strings of glass along the margins of which conversion to cristobalite has begun. × 100 diams.

b.—More completely altered ganister fragment from used roof brick showing small clear areas of unconverted quartz in a mass of cristobalite, tridymite and fine magnetite. The ground-mass of the brick is to be seen at the edge of the field as a coarser aggregate of tridymite and magnetite. × 30 diams.

Near the cooler part of the brick a light-brown glass makes its appearance in increasing proportion between the tridymite crystals, and through this the magnetite is scattered in dendritic growths (Pl. VI, fig. 2). Simultaneously there is a notable increase in the lime and alumina-content (cf. Table, p. 64). It seems clear that the lime has been derived from the hotter parts of the brick, and its migration has been variously explained. As pointed out by le Chatelier, this zone may conceivably be a source of danger if the temperature of the brick is suddenly raised. So great a change, however, rarely if ever occurs in ordinary working, and a greater source of danger probably lies in the iron-rich part of the tridymite zone.

At the limit of penetration of iron there is a sharply-defined line beyond which no magnetite can be seen, the ground-mass being penetrated only by the pale-brown glass which diminishes in amount till the bleached but otherwise unaltered portion of the brick is reached. In the brick shown in Pl. V the region containing brown glass extends for a distance of about half-an-inch beyond the limit of the magnetite, and forms a well-defined additional zone, but in most bricks the limit of magnetite is quickly succeeded by the unaltered brick.

Influence of Gas-conditions on the Corrosion of Silica-structures.

The proportion of ferric oxide present in a melt at high temperatures is dependent on the composition of the melt, on the composition of the surrounding gases, and on the temperature. In the furnace-chamber itself the surface-layer is exposed to burnt gases and is very hot; a considerable amount of the iron will probably be present as FeO. In the surface-layer of the uptakes the temperature is perhaps somewhat lower and certainly the proportion of iron is greater. Here, however, the conditions differ essentially between the air- and gas-passages, the latter being corroded at a considerably greater rate. This is probably due largely to the fact that in the presence of a reducing gas much of the ferric oxide in the melt is reduced, with the formation of fayalite ($2FeO.SiO_2$). This compound has a marked 'thinning' action on the fused layer, which consequently is able to penetrate and attack the brick at a greater rate.

A similar condition must be taken account of when considering attempts that have been made to produce a brick with iron oxide as an essential constituent. Such a brick can be heated (presumably under oxidising conditions) to a temperature that approaches the softening point of a pure silica-brick, and at lower temperatures is quite strong, no doubt because much of the iron is present as magnetite. In a reducing atmosphere, however, the brick will become heavily slagged and will be exposed to the danger of distortion. Local ferruginous patches have a deleterious effect even in the burning of an ordinary brick, where probably their harmful effect may be attributed to the introduction of irregularities in expansion that lead to weakness in the furnace.

In view of the great difference in the degree of corrosion of the gas- and air-ports, it would seem that the oxidising character of

the gas-mixture used must play an important part in the preservation of the lining itself. Even if the temperature were not raised, a mixture rich in gas would be likely to ' burn down ' the brickwork at an increased rate.

Physical Constants in Relation to Practice.

The widespread use of silica-refractories has been determined mainly by two distinctive properties. On the one hand melts derived from silica are exceptionally viscous and afford a thick protective fluid layer; on the other hand the melting-point curve is remarkably flat and consequently at high temperatures a large proportion of silica remains in the solid state even in the presence of much impurity. Another important property is the high reflecting power of melted silica, which only permits a certain proportion of the incident radiation to penetrate the surface; the heat is ' thrown off ' and thus the heat loss through the brickwork is diminished while the intensity of radiation in the furnace is maintained. Reference has already been made to the fluid layer; the viscosity of this layer is of the utmost importance, and the thinner it is, so much the less durable will be the brick. In this connexion mention may be made of a trial of aluminous bricks in which the observed greater corrosion was almost certainly due directly to the thinning action of the alumina.

Concerning the heat-capacity and conductivity of the brick little need be said. These properties increase with the density, bricks for insulating purposes being made as light as possible. For the steel furnace, however, the advantages to be gained from efficient cooling seem to outweigh any heat-economy that might be obtained by the use of light bricks. Moreover, the weight of the brick is determined by other more important considerations that will be given below.

Porosity and Density.

The demands made upon the silica-brick in a furnace lining will perhaps be more clearly understood if we consider a substitute that has been proposed for the pure brick. After service, the roof-brick in its outer zones contains an average of 20 per cent. of iron oxide, mainly as magnetite. For practical purposes, therefore, the furnace might be regarded as being built of magnetite bricks, and it has been suggested by several writers that a ferruginous brick might prove a successful substitute for one of pure silica, but whether the improvement in strength would outweigh the loss in resistance to corrosion is rendered doubtful by the following considerations.

The corrosion of the roof takes places through the formation of a viscous slag that runs slowly from the surface of the bricks. An analysis of this slag is as follows :—

SiO_2, 65·3; Fe_2O_3, 31·7; Al_2O_3, 1·2; MnO, 0·7; CaO, 0·9 per cent.

Now during the corrosion of an ordinary nine-inch brick, the removal of three inches of the brick corresponds with a loss in weight of about 3 lbs. of silica. The iron oxide that has combined with this silica to form a slag of the above analysis

must, therefore, weigh about $1\frac{1}{2}$ lbs. A further amount of iron is held in the pores of the brick, especially in the tridymite zone, and from the description and analysis already given (page 64) it can be seen that this will amount to, roughly, $\frac{1}{2}$ lb. The total iron oxide discharged upon the brick during the period considered has, therefore, been about 2 lbs., and of this the iron held in the pores forms a considerable proportion. The porosity is, therefore, by no means a negligible factor in the preservation of the brick. Turning again to the fluxed layer, it will be seen that, since the rate of discharge of iron upon the surface is dependent solely upon furnace-conditions, the rate of corrosion will depend simply upon the viscosity of the slag—this, again, with a pure brick, depends only on the furnace-conditions—and upon the amount of silica in each cubic inch of the brick. Under the same conditions, the denser the brick, the greater will be the amount of slag that it can form and the longer the period of service before the first three inches have been fluxed away.

In a brick identical in structure with the black zone of the roof-brick the added magnetite would occupy the pores of the brick, and so would not diminish the silica-content: nevertheless, the removal of this iron would necessitate the formation either of more slag, for which no silica is available, or of a thinner slag, accompanied by more rapid corrosion. In the case of a magnetite-brick made by the ordinary process, the porosity would be higher and the magnetite would occupy the place of a part of the silica, so that the silica-content of the brick as a whole would be less, a condition even more undesirable than that of a soaked brick.

For use in the steel-furnace, then, it seems clear that, setting aside the question of spalling, the main consideration is the concentration in each brick of the greatest possible weight of silica. Density and porosity are to a great extent mutually exclusive properties, between which a choice must be made, but without doubt a high density is the more important. On this account overburning, which lowers the density, is undesirable. Quartz has a greater density than other forms of silica, and, provided that the other properties are satisfactory, the best brick is to be expected from the use of as large a proportion as possible of a ganister that does not undergo conversion during burning. This condition is fulfilled to a conspicuous degree in the bricks made from the Sheffield ganister.

In the bricks used for the ports, where the refractory character is most severely tested, the porosity is important, for the whole structure at this point becomes soaked with slag, and the amount of foreign matter brought in depends upon the porosity. The strength of the brickwork is dependent, of course, upon the amount of free silica present at furnace-temperatures, and it is evident that the bricks for this part of the structure will increase not only in durability but in strength, in proportion as their porosity diminishes.

Spalling.

The minor improvements in physical properties that can be produced in a commercial brick are limited by the necessity for guarding against certain physical defects that arise only too

easily when any departure is made from standard methods of preparation. The permanent expansion and strength have already been discussed, but there remains an important defect concerning the causes of which but little is known. When a new furnace is first brought to a red heat, even with all reasonable care, it not infrequently happens that the exposed ends of many of the bricks crack off at a depth of one inch or more and fall to the bottom of the furnace. This is termed ' spalling.' In general terms it may be attributed to the inability of a new brick to withstand the stresses produced by the expansion of the surface-layer, and it would seem that a comparison of the expansions at low temperatures with the strength of the brick should throw light on the cause. It has been suggested that the large expansion of cristobalite near 270° C. is the determining factor, but unfortunately, although but little cristobalite is present in the majority of bricks, the defect is still too frequently met with. This question offers one of the most important subjects for investigation in connection with silica-bricks.

Various laboratory tests have been proposed in place of actual trial in the furnace; they rely generally upon an imitation of furnace conditions, and, while yielding characteristic results, do not throw direct light on the causes of spalling. After being heated to 600° C. most bricks show a marked diminution in crushing strength, and this has been used as a test. Evidently the heating causes numerous cracks within the brick, and it is clear that there is but little margin of strength. A property that seems to have escaped investigation in this connexion is the elasticity. The differential heat expansion between two layers is ascertainable from the expansion curve, but the value of the shearing stresses developed will depend on the elasticity. A substance may show a high maximum stress, but if it is deficient in elasticity the danger limit will quickly be reached under unequal thermal expansion.

The practical importance of spalling can hardly be exaggerated. One of the main reasons for the advocacy of an iron-silica brick for the lining is the elimination of spalling, and it must be admitted that the probable reduction in the life of the furnace through the causes mentioned on page 70 might well be more than compensated by the elimination of the even more serious damage that results from spalling, by which some inches may be lost from the surface in a few minutes.

CHAPTER VIII.

Hearth Sands.

The refractory hearths and banks of the acid furnaces are made from pure silica-sands. An account of the physical characters and occurrences of numerous sands suitable for this purpose has recently been given by Professor P. G. H. Boswell in 'British Resources of Refractory Sands for Furnace and Foundry Purposes,' Part I, 1918[1]; further information as to occurrences will be found in Vol. VI of the Special Reports.

Given a high silica-percentage, the main factor that determines the value of a sand for employment in steel furnaces is the shape and size of the component grains, and it is a well-established fact that in the sands used even-grading is an almost constant feature. The size of grain most usually employed would seem to be from 0·1 to 0·3 mm., but some variety in size and shape is permitted.

Even-grading, when not a feature of the natural sand, can be produced by screening or washing, and at the same time undesirable constituents, especially clay, can be partly eliminated.

The sands are mainly composed of subrounded fairly pure quartz-grains, which are answerable for the bulk of the silica found on analysis. Other constituents, which in the best sands form only a small percentage, consist of potash felspars, visible muscovite, ilmenite and magnetite. Some other minerals, such as rutile, tourmaline, garnet, cyanite, etc., are often present in fractions of one per cent., but in British sands an unsatisfactory analysis is nearly always due to the presence of the common substances enumerated above.

In addition to the impurities present as distinct mineral grains, there often occurs a variable amount of interstitial clay-substance, including finely-divided micas, kaolin, and allied minerals. Further, the surfaces of the larger grains and the interstitial matter may be coated and stained by hydrated oxides of iron. The iron present may be reduced by washing out ferruginous clay-substances, but the coating and staining on the larger grains cannot be eliminated entirely.

The chemical analyses, quoted on pages 73–75 from various trade sources, may be considered as representative of the sands in common use in this country. They show a silica-percentage ranging between such limits as 95 and 99 per cent., the average being about 98. A fall in the percentage is usually counterbalanced by an increase in the figures for alumina and water, pointing to the presence of an increased proportion of hydrated aluminum silicates.

The alumina, except in certain sands that contain a moderate proportion of detrital cyanite (aluminium silicate) or are highly felspathic, is usually present as interstitial clayey matter, and thus a rise in the percentage of alumina generally accompanies unequal grading. Felspar is indicated by increased percentages of alkalies and alumina, together with a relative diminution in the percentage of combined water.

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[1] Published at the Instruction of the Ministry of Munitions of War by the Imperial College of Science and Technology and the University of Liverpool. 8vo. London.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	
SiO_2	98·97	92·67	99·04	99·47	98·77	99·80	99·39	98·76	99·05	99·59	SiO_2
TiO_2	·04	·26	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	TiO_2
Al_2O_3	·46	4·62	·84	·24	·73	·32	·48	·37	·23	·25	Al_2O_3
Fe_2O_3	·02	·05	·03	·002	·01	·03	·02	·03	·14	·21	Fe_2O_3
CaO	·10	·14	·10	·29	·14	n.d	n.d	·17	·31	n.d.	CaO
MgO	·07	·09	·18	trace	trace	n.d	n.d	·10	·08	n.d.	MgO
K_2O	·08	·19	none	none	none	none	none	·04	none	n.d.	K_2O
Na_2O	none	none	none	none	none	none	none	none	none	n.d.	Na_2O
Loss on ignition ...	·34	1·88	·19	·20	·43	·22	·13	·33	·31	·27	Loss on ignition
Total	100·08	99·90	100·38	100·202	100·08	100·37	100·02	99·80	100·12	100·32	Total.

I.—Mold, Washed.
II.—Mow Cop.
III.—Huttons Ambo, washed.
IV.—Fairlight (Ashdown Sands).
V.—Ashurstwood (Tunbridge Wells Sands).
VI.—Aylesbury, best quality.
VII.—Aylesbury, washed.
VIII.—Aylesbury, bulk sample.
IX.—Leighton Buzzard (Arnold's pits), washed.
X.—Leighton Buzzard (Arnold's pits), unwashed.

	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	XXIII.	XXIV.	XXV.
SiO_2	96·20	88·20	97·00	98·26	97·60	97·60	98·71	93·80	95·20	97·76	95·00
Al_2O_3	2·00	7·39	2·57	1·39	1·67	1·15	·52	3·30	3·15	1·64	2·90
Fe_2O_3	trace	1·61	·07	·05	·65	·20	·29	trace	1·25	—	1·70
CaO	·38	·43	·32	·26	trace	·15	·31	1·44	—	·15	·90
MgO	·10	trace	·04	·03	trace	·12	·09	trace	·20	·15	trace
Combined Water ...	—	—	—	—	—	—	·08	—	—	—	—
Alkalies	—	—	—	—	—	—	—	·96	—	—	—
Loss on ignition ...	·30	1·40	—	—	—	·75	—	—	·20	—	—
Total	98·98	99·03	100·00	99·99	99·92	99·97	100·00	99·50	100·00	99·70	100·50

XV.—Sample from Smithstone, Kilwinning. Analysis on dry sample ... Anal. J. Gibson.
XVI.—Sample from Blackstone Farm Burn, West Killside ... ... Anal. J. Gibson.
XVII.—Ground Sandstone, Glenyards, near Greenhill (raw) ... ... Anal. communicated by R. Mather, Esq., Provanhall, Stepps.
XVIII.—Ground Sandstone, Glenyards, near Greenhill (washed) ... Anal. communicated by R. Mather, Esq., Provanhall, Stepps.
XIX.—Ground Sandstone, Breich Quarry, near Fauldhouse ... ... Anal. communicated by The Steel Company of Scotland.
XX.—Sandstone, roof of Main Coal, Argyll Colliery, Machrihanish ... Anal. D. Colville & Sons.
XXI.—Sandstone, roof of Main Coal, Argyll Colliery, Machrihanish ... Anal. The Campbeltown Coal Co.
XXII.—Natural (blown) Sand, Arden, Argyllshire ... ...
XXIII.—Loch Libo Quarry, Caldwell ... ... Anal. communicated by The Steel Company of Scotland.
XXIV.—Loch Libo Quarry, Caldwell (washed) ... ... Anal. communicated by The Steel Company of Scotland.
XXV.—Ground Sandstone, Blochairn Quarry ... ... Anal. communicated by The Steel Company of Scotland.

	XI.	XII.	XIII.	XIV.
SiO_2	90·30	98·54	97·640	95·73
TiO_2	·31	—	—	—
Al_2O_3	4·51	·61	·181	3·16
Fe_2O_3	1·02	·26	·039	·41
FeO	·21	—	—	—
CaO	·15	·22	trace	·02
MgO	·23	—	trace	—
H_2O +...	1·72	—	·072	·19
H_2O −...	·52	—		
Na_2O	·12	—	—	·49
K_2O	·75	—	—	
Loss on ignition ...	—	·37	1·930	—
Total	99·84	100·00	99·862	100·00

XI.—Huttons Ambo, moulding sand.

XII.—Washed Lynn Sand. Analysis communicated by H. Mead & Co., Ltd., Hull.

XIII.—Cave Sand. Analysis communicated by H. Mead & Co., Ltd., Hull.

XIV.—Plastering Sand, Edward's Quarry, Bawtry. Anal. H. Russell. Worksop.

	XXVI.	XXVII.	XXVIII.	XXIX.	XXX.	XXXI.
SiO_2	98·76	98·40	97·40	99·862	97·95	99·8500
Al_2O_3	·64	·35	·57	·025	·65	·0202
Fe_2O_3	trace	1·00	·17	·020	·94	·0030
CaO	·10	nil	·14	nil	·23	·0108
MgO	·16	·20	·10	·056	·10	—
K_2O	·46	—	1·41	nil	—	—
Na_2O						
Combined water	·20	—	—	—	—	—
Loss on ignition	·25	—	·21	·937	—	—
Total ...	100·57	99·95	100·00	100·900	99·87	99·8840

XXVI.—Typical Belgian Sand. Analysis communicated by D. Colville & Sons, Ltd., Motherwell.

XXVII.—Belgian Sand. Analysis communicated by The Steel Company of Scotland.

XXVIII.—Dutch Sand, No. 1. Analysis communicated by H. Mead & Co., Ltd., Hull.

XXIX.—Dutch Sand, A. Analysis communicated by H. Mead & Co., Ltd., Hull.

XXX.—Dutch Sand. Analysis communicated by The Steel Company of Scotland.

XXXI.—Fontainebleau Sand. Analysis communicated by H. Mead & Co., Ltd., Hull.

Use of Sands in the Furnace.

Concerning the method of use of the sands, little detailed information is available, but it may be of interest to trace the changes they undergo during service and to compare them with the corresponding changes in other parts of the furnace.

The bottom is built up in successive layers upon the stepped brickwork of the furnace-structure. The first layers contain a large proportion of silica-rock; this is followed by layers containing more pure sand, which is banked against the side of the

furnace to form the hearth itself in which the charge is to be melted. The total thickness may be three feet. These layers are 'burnt in' successively, the temperature being raised until a sufficient degree of fritting has been attained. This is accompanied by the conversion of some of the quartz into tridymite and cristobalite. The conversion to tridymite and consequent knitting together of the hearth (Plate VII, fig. 3) is greatly accelerated by the presence of iron oxide, and slag is sometimes added for this purpose before the first charge is made. In any case, as soon as the furnace is used the slag rapidly penetrates the porous newly-made hearth. It seems at first sight remarkable that, while the sand used is required to have a degree of purity not lower generally than from 96 to 98 per cent. of silica, the hearth itself in use contains only 70 per cent., even in the hottest layer. The 'bank' above the surface of the bath has a higher percentage, and approximates in composition to the surface-layers of the brickwork, but is still much penetrated by iron oxide. The reason for this anomaly would seem to be as follows. The surface-layer of the hearth requires repairs throughout the whole period of service; after each charge has been 'tapped out' the hearth is examined, holes are filled with new sand, and the banks are repaired by throwing upon them sand that assumes a slope representing the angle of rest of the grains. It is an essential function of the sand to absorb the residue of slag left on the surface of the hearth and so prevent the formation of local patches deficient in silica, which would give rise to weakness during the next heat. To do this a sand free from slag-forming constituents is necessary, not only because these would occupy the pores into which the surface slag should penetrate, but because even a small proportion would seal the interstices and leave the new patch in a more or less impermeable condition. The patch, when successfully made, becomes a part of the hearth, and so it results that the average composition of an old furnace-bottom is that of a pure sand soaked with the residual slag.

The 'Banks.'—At the level of the surface of the melted charge, the sides of the hearth are in direct contact with the slag, and it is at this point, termed the 'wash,' that the 'cutting' action of the slag is most strongly evidenced.

The 'bank' above the 'wash' is rather higher in silica-content than the bottom itself. It is exposed directly to the furnace gases and has a structure of granular cristobalite with interstitial melt which is similar to that of the surface-layer of the brickwork The requirements with respect to rigidity are much the same as for the brick itself when used in the 'blocks,' and it is evident that purity of sand is a necessity, though the presence of a considerable amount of alumina may be permissible. The main objection to alumina appears to be that in the presence of iron oxide it yields too fluid a slag; aluminous structures which may be perfectly refractory are therefore peculiarly subject to the 'cutting' action of any slag or oxide present. Exact data for the comparison of the behaviour of various sands are lacking, but it appears that alumina is less active than other impurities in softening the bank.

The Furnace-bottom.—Below the 'wash,' where the metal is in direct contact with the hearth, the temperature is, of course, distinctly lower than that of the 'bank.' Nevertheless it necessarily approaches that of the melted steel, which may be as high as 1,600° to 1,650° C. at certain parts of the heat. This is well above the transition-point to cristobalite, and accordingly the surface-layer consists of rounded crystals of this mineral embedded in slag. The proportion of iron oxide is higher than that in the corresponding zone of the roof-brick, and it is indeed remarkable that sufficient rigidity can be obtained. This zone is apparently only two or three inches in thickness, a fact which suggests strongly that the layer of steel in contact with the hearth is not quite at the full temperature of the melt. Beyond the narrow cristobalite zone the hearth consists of interlacing crystals of tridymite, often twinned, and it is to this structure that its rigidity is mainly due. The analysis is remarkably similar to that of the black zone of a roof-brick. The interstices are filled with slag, but since the iron is reduced to a much greater degree than in the roof-brick, this crystallises as fayalite on cooling. Towards the exterior of the furnace the proportion of fused slag diminishes and fragments of unaltered ganister are found surrounded by fringes of tridymite. The slag may penetrate to the stepped brickwork on which the sand bottom is made. It is clear that in the lower part of the hearth little demand is made on the refractory character of the sand, but that impurities will in general have a weakening influence in that they contribute to the formation of slag. In spite of its loose texture the bottom frequently cracks when the furnace is cooling, and admits metallic iron or slag. In the latter case the tridymite crystals formed on cooling can be distinguished by their lath-shaped section, as in the roof-brick.

It is important to observe that throughout the interior of the hearth the iron is principally in the ferrous state. The metal that penetrates is, therefore, not rapidly oxidised, and is consequently less immediately harmful in its effect; in fact the presence of solid metal in the colder parts might be regarded as a source of strength, but only so long as the iron does not become oxidised.

It will be understood from the foregoing sketch of the hearth-structure, that the properties required in a hearth-sand are connected rather with the details of the manipulation of the sand than with the final composition of the hearth.

Mention has been made of the 'angle of rest,' which determines the slope of the sides of the bath. A high angle is important, and, other things being equal, an angular sand is preferable in this respect.

A property that is of the highest interest is the concentration of silica obtained in the fired refractory before slag-penetration occurs. In the case of roof-bricks, the durability of the brick under a constant attack by slagging, is determined by the mass of silica that must be removed before the brick becomes too thin, In the hearth, wear does not take place to the same extent, but since the strength of the hearth is dependent on the proportion of

free tridymite at furnace-temperature, a similar consideration will apply. In the presence of only 70 per cent. of silica there can be but little margin for any decrease in the silica-content. This is dependent upon the porosity of the newly-made hearth or patch, for the amount of slag that penetrates is the amount required to fill the pores. Clearly it is essential that the sand should be of such a character that it will pack as closely as possible when thrown upon the hearth. Great differences in porosity can be produced by suitable grading, but these differences are only fully developed when the sand is 'shaken down.' No such action is possible in the furnace and for this reason the good effect that might be hoped for from the use of a mixed grading is largely nullified. It will readily be seen that the presence of a small amount of fine material in a coarse sand might actually increase the porosity of the sand before shaking, on account of the separation of the grains by the fine particles, and it is of interest to note that the sands which have proved satisfactory, are those that have a uniform grade and attain their full density without being 'shaken down.'

It is doubtful whether any good purpose would be served by increasing the proportion of the silica in the hearth, as might be done if a closer packing could be produced in the sand. The quantity of slag to be absorbed seems to balance well with the porosity of the sand used for repairing after each heat, and it seems probable that any disturbance of this relation would lead to the formation of fluid patches that would be a source of trouble during the subsequent heat.

CHAPTER IX.

Dolomites.

Introduction.

The name dolomite, as a mineral designation, is used for a definite compound of calcium and magnesium carbonates in equal molecular proportions. As a rock-name it embraces a series of calcareous rocks into the composition of which magnesium carbonate enters as a minor constituent in varying proportions. Pure dolomite-rock has approximately the chemical composition of the mineral.

Dolomites and dolomitic limestones mainly occur as bedded deposits of Carboniferous and Permian age, and are common in the North of England, Derbyshire, South Wales, and the Forest of Dean. Vein-dolomites, due to the introduction of magnesia into limestones along joints or other lines of weakness, are of less general occurrence, but are often of considerable purity.

The bedded dolomites may have a fairly constant chemical composition when followed laterally, but vertically they vary progressively or by alternation within narrow limits. Their chemical composition, therefore, has merely local significance.

Generally they are of a pale- to dark-buff colour, the tint being dependent mainly upon the content of ferrous iron in the form of carbonate, or of ferric iron as oxides. Occasionally carbon may impart a grey tint.

Texturally the purer rocks consist of an interlocking mass of dolomite crystals. In the more compact varieties these crystals are from 0·02 to 0·5 mm. in diameter, but in the coarser varieties the individual crystals are plainly visible to the unaided eye and may measure a millimetre in greatest dimension.

In the less pure rocks, especially those which contain a considerable proportion of lime over and above that required by the composition of pure dolomite, calcite either exists as a constituent of the crystalline mozaic, or builds large plates into which project, or in which are included, well-formed crystals of dolomite. Calcite generally exists as an interstitial crystalline matrix to a mass of dolomite crystals, and the cavernous nature of many dolomitic rocks is in part due to the removal of calcite by reason of its greater solubility in carbonated waters.

The ' insoluble residue ' from dolomites is extremely variable in amount, but restricted in composition. It is dependent rather upon the original character of the limestone from which the dolomite has arisen than upon the degree of dolomitization, or, in other words, upon the ratio of calcium carbonate to magnesium carbonate. It varies from almost nil to 14 per cent., but in the majority of dolomites employed for refractory purposes seldom

exceeds 2 or 3 per cent., and is generally much less. In composition it consists essentially of quartz with some felspars and mica, and a variable amount of crypto-crystalline silica and argillaceous material. The quartz may occur as finely-angular detrital grains, more or less evenly distributed, or as small, well-shaped crystals due to secondary growth. Mica is present usually in small quantity only and as minute flakes. Felspar is sometimes a prominent constituent of the insoluble residue, but is generally insignificant. The clay-content is an important factor; it is usually greater in the fine-textured rocks than in those with well-marked crystalline structure. Argillaceous matter is represented in some quantity in almost all the rock-analyses given on pp. 81–88.

Chemical Analyses.

A pure dolomite-rock should be an aggregate of dolomite crystals, have the composition of the pure mineral, and should thus contain 54·35 per cent. of calcium carbonate and 45·65 per cent. of magnesium carbonate, the ratio of CaO to MgO being 1 to 1·4. It will be seen from the following analyses of some of the best-known dolomitic rocks that they seldom reach this degree of purity, and there is generally a notable excess of CaO over that required by the theoretical ratio of CaO to MgO. This excess is determined by the degree of dolomitization and by the amount of interstitial or patchy calcite present in the rock.

Alumina, which has been determined apart from the insoluble residue, exists presumably as hydrated aluminium silicates or as hydrated alumina, compounds which are decomposed by acids and which are common constituents of argillaceous sediments. It will be seen that the percentage of alumina bears no relation to that of insoluble residue, but is governed to a certain extent by the texture, the rocks of finer grain and denser structure being more highly aluminous than the others.

Iron, except in those rocks that have been subjected to the action of oxygenated waters, usually exists in the ferrous state, combined with carbon dioxide to form chalybite, or it may enter into the constitution of the dolomite itself.

ANALYSES OF DOLOMITES.—YORKSHIRE.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	
Lab. No.	555	556	557	558	559	563	572		Lab. No.
Slice No.	E. 11732	E. 11733	E. 11734	E. 11735	E. 11736	E. 11746	E. 11795	E. 9281	Slice No.
Insoluble residue ...	·11	·47	·31	·44	·65	3·98	·12	·98	Insoluble residue
SiO_2	·14	·22	·50	·21	·35	·81	·07	—	SiO_2
Al_2O_3	1·90	1·37	·28	·02	1·07	1·96	3·10	·76	Al_2O_3
Fe_2O_3	·49	·38	1·65	1·73	·05	·31	1·28	·12	Fe_2O_3
FeO	·17	·42	·51	·22	·31	·54	·48	·66	FeO
MnO	·02	·04	·05	·03	·06	·04	·06	—	MnO
CaO	30·07	29·50	30·39	30·35	30·08	29·38	32·65	29·21	CaO
MgO	20·75	21·02	20·16	20·46	20·80	18·62	17·21	21·16	MgO
H_2O at 105°C. ...	·01	·05	·04	·02	·05	·10	·08	·20	H_2O at 105°C.
H_2O above ,, ...	·27	·22	·32	·36	·36	·47	·52	·51	H_2O above ,,
FeS_2	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	nt. fd.	—	FeS_2
SO_3	·61	·99	·18	·41	·20	·20	nt. fd.	—	SO_3
C	·03	·04	·11	·01	·02	·02	nt. fd.	—	C
CO_2	46·02	45·84	46·09	46·08	46·15	43·63	44·45	46·41	CO_2
Total	100·59	100·56	100·59	100·34	100·15	100·06	100·02	100·01	Total
$CaCO_3$	52·94	51·46	54·04	53·70	53·71	52·21	58·32	52·16	$CaCO_3$
$MgCO_3$	43·36	43·93	42·13	42·76	43·37	38·93	35·99	44·22	$MgCO_3$
$FeCO_3$	·27	·68	·82	·36	·50	·87	·77	1·06	$FeCO_3$
$MnCO_3$	·03	·06	·08	·04	·09	·06	·09	—	$MnCO_3$
$CaSO_4$	1·04	1·68	·31	·69	·34	·34	nt. fd.	—	$CaSO_4$

ANAL. E. G. RADLEY.

ANALYSES OF DOLOMITES.—DURHAM.

	IX.	X.	XI.	XII.	XIII.	XIV.	
Lab. No.	564	565	566	567	568	569	Lab. No.
Slice No.	E. 11747	E. 11748	E. 11749	E. 11750	E. 11751	E. 11753	Slice No.
Insoluble residue ...	·27	·20	·45	2·23	1·29	·91	Insoluble residue
SiO_2	·19	·06	·06	·41	·30	·21	SiO_2
Al_2O_3	1·15	2·22	1·84	1·68	2·49	1·65	Al_2O_3
Fe_2O_3	·12	·12	·19	·26	·68	·33	Fe_2O_3
FeO	·28	·17	·22	·31	·31	·25	FeO
MnO	·04	·04	·02	·02	·05	·04	MnO
CaO	34·17	30·84	30·63	30·56	31·42	32·13	CaO
MgO	17·64	19·72	20·22	19·96	18·26	18·52	MgO
H_2O at 105°C.	·04	·04	·02	·10	·07	·07	H_2O at 105°C.
H_2O above ,, ...	·36	·82	·36	·55	·56	·42	H_2O above ,,
SO_3	·47	·17	nt. fd.	nt. fd.	nt. fd.	nt. fd.	SO_3
C	·03	·04	·02	·06	·05	·03	C
CO_2	46·01	45·75	46·27	43·99	44·60	45·61	CO_2
Total	100·77	100·19	100·30	100·13	100·08	100·17	Total.
$CaCO_3$	60·42	54·86	54·70	52·79	56·12	57·37	$CaCO_3$
$MgCO_3$	36·87	41·21	42·27	41·72	38·16	38·71	$MgCO_3$
$FeCO_3$	·45	·27	·36	·50	·50	·41	$FeCO_3$
$MnCO_3$	·06	·06	·03	·03	·08	·06	$MnCO_3$
$CaSO_4$	·81	·29	nt. fd.	nt. fd.	nt. fd.	nt. fd.	$CaSO_4$

ANAL. E. G. RADLEY.

I.—Permian Dolomite. Sprotborough Quarry (Warmsworth Cliff), Yorkshire. 1 inch map 87.

II.—Permian Dolomite. Sprotborough Quarry (Warmsworth Cliff), Yorkshire. 1 inch map 87.

III.—Permian Dolomite. Below geode rock. Hampole Quarry, Yorkshire. 1 inch map 87.

IV.—Permian Dolomite. Top of bed, 18 in. below clay, Hampole Quarry, Yorkshire. 1 inch map 87.

V.—Permian Dolomite, about "10 ft. down" Roche Abbey Quarry, Yorkshire. 1 inch map 100.

VI.—Permian Dolomite. Upper 50 ft. of quarry. Kiveton Park Quarry, Yorkshire. 1 inch map 100.

VII.—Carboniferous Dolomite. Threshfield Quarries, Skipton, Yorkshire. 1 inch map 61.

VIII.—Permian Dolomite. Anston Quarry, Yorkshire.

IX.—Permian Dolomite, "Top Shell," Coxhoe Quarries, Old Side, Quarrington Hill, Durham. 1 inch map 27.

X.—Permian Dolomite, 20 ft. to 26 ft. below bearing (Hard Blue), Coxhoe Quarries, Quarrington Hill, Durham. 1 inch map 27.

XI.—Permian Dolomite, 26 ft. to 46 ft. below bearing (Bottom Hard), Coxhoe Quarries, Quarrington Hill, Durham. 1 inch map 27.

XII.—Permian Dolomite (Soft), bottom 10 ft. of section, Coxhoe Quarries, Quarrington Hill, Durham. 1 inch map 27.

XIII.—Permian Dolomitic Limestone, Lower 20 ft. of the 80 ft. of dolomite above transition beds, Raisby Hill Quarries, Durham. 1 inch map 27.

XIV.—Permian Dolomite. Top good limestone, 6 ft. thick, Eppleton Quarry, Hetton Down, Durham. 1 inch map 21.

Analyses of Dolomites.—Derbyshire.

	XV.	XVI.	XVII.	LIV.*
Lab. No.	560	561	571	—
Slice No.	E. 11737	E. 11738	E. 11756	—
Insoluble residue ...	·34	1·93	·05	—
SiO_2	·09	·30	·01	3·1
Al_2O_3	·76	1·84	·67	1·45
Fe_2O_3	·01	·01	·06	
FeO	·39	·34	·28	
MnO	·05	·02	·07	
CaO	30·25	30·58	33·51	28·65
MgO	20·83	20·22	18·55	19·58
H_2O at 105°C. ...	·03	·07	·01	1·97
H_2O above ,, ...	·26	·23	·27	
SO_3	·61	·44	nt. fd.	
C	·01	·01	·02	
CO_2	46·43	44·05	46·56	45·2
Total	100·06	100·04	100·06	99·95
$CaCO_3$	53·25	54·05	59·85	—
$MgCO_3$	43·55	42·27	38·77	—
$FeCO_3$	·64	·55	·45	—
$MnCO_3$	·08	·03	·11	—
$CaSO_4$	1·04	·75	nt. fd.	—

Anal. E. G. Radley.

XV.—Permian Dolomite. Bed just below top rag. Steetley, near Shireoaks, Derbyshire. 1 inch map 101.

XVI.—Permian Dolomite. "Cank" = the bottom bed. Steetley, near Shireoaks, Derbyshire. 1 inch map 101.

XVII.—Carboniferous Dolomite. Harboro' Rocks, Brassington, Derbyshire. 1 inch map 111.

LIV.—Dolomitic Limestone, Carboniferous Limestone Series. Cumberland Cavern, Matlock Bath, Derbyshire. (* Analyst F. Rutley).

Analyses of Dolomites.—Leicestershire, Nottinghamshire and Shropshire.

	XVIII.	XIX.	XX.	XXI.	XXII.	XXIII.
Lab. No.	579	562	573	574	575	576
Slice No.		E. 11739	E. 11741	E. 11742	E. 11743	E. 11744
Insoluble residue ...	·63	·95	2·32	·73	·05	1·68
SiO_2	·01	·26	·44	·17	·06	·32
Al_2O_3	·69	1·47	2·00	1·28	·82	2·82
Fe_2O_3	·04	·09	·32	·08	·33	·81
FeO	·59	·42	·17	·11	·08	·08
MnO	·07	·02	·04	·05	·04	·03
CaO	30·13	30·31	31·97	31·23	31·11	30·41
MgO	20·65	20·00	17·56	19·82	20·35	18·72
H_2O at 105° C. ...	·10	·05	·23	·11	·11	·17
H_2O above ,, ...	·60	·32	·66	·46	·58	·69
SO_3	nt. fd.	·42	nt. fd.	nt. fd.	nt. fd.	nt. fd.
C	·01	·05	·07	·02	·03	·07
CO_2	46·61	45·65	44·27	46·26	46·63	44·30
Total	100·13	100·01	100·05	100·32	100·19	100·10
$CaCO_3$	53·81	53·58	57·10	55·78	55·56	54·31
$MgCO_3$	43·17	41·81	36·70	41·43	42·53	39·12
$FeCO_3$	·96	·68	·27	·18	·13	·13
$MnCO_3$	·11	·03	·06	·08	·05	·08
$CaSO_4$	nt. fd.	·72	nt. fd.	nt. fd.	nt. fd.	nt. fd.

Anal. E. G. Radley.

XVIII.—Carboniferous Dolomite. Near bottom of quarry, side near school, Breedon Hill Quarry, Leicestershire. 1 inch map N.S. 141 ; 6 inch map, Liecester 9. S.E.

XIX.—Permian Dolomite. W. Sill's Quarry, Pleasley Junction, Notts. 1 inch map 112.

XX.—Carboniferous Dolomite. Whitehaven Quarry, Porthywaen, Llynclys, near Oswestry, Shropshire. 1 inch map 137.

XXI.—Carboniferous Dolomite, "Stinker," same locality as XX.

XXII.—Carboniferous Dolomite, "Red Bed," same locality as XX.

XXIII.—Carboniferous Dolomite, "Buggeroo," same locality as XX.

ANALYSES OF DOLOMITES.—GLOUCESTERSHIRE.

	XXIV.	XXV.	XXVI.	XXVII.	XXVIII.	XXIX.	XXX.	
Lab. No.	582	583	594	596	597*	598†	599	Lab. No.
Slice No.	—	—	E. 11745	E. 11839	E. 11861	E. 11862	E. 11863	Slice No.
Insoluble residue ...	1·06	·88	2·82	4·46	3·73	1·46	·45	Insoluble residue
SiO_2	·09	·94	·12	·22	·18	·14	·15	Si_2O
Al_2O_3	1·25	2·93	·68	2·11	1·77	2·53	·97	Al_2O_3
Fe_2O_3	·21	nt. fd.	·18	1·78	·32	·13	·03	Fe_2O_3
FeO	·39	1·22	1·10	·17	·79	1·28	·71	FeO
MnO	·03	·05	·03	·03	·06	·08	·07	MnO
CaO	31·03	29·75	32·16	29·83	30·73	30·82	30·49	CaO
MgO	19·33	18·86	17·33	17·70	17·70	18·60	20·36	MgO
H_2O at 105° C.... ...	·07	·11	·14	·38	·33	·14	·15	H_2O at 105° C.
H_2O above ,, ...	·55	·45	·48	·54	·54	·36	·58	H_2O above ,,
SO_3	·39	nt. fd.	·25	·12	·15	·18	nt. fd.	SO_3
C	·17	·05	·02	·05	·01	·03	nt. fd.	C
CO_2	45·46	44·70	44·72	42·78	43·87	44·40	46·65	CO_2
Total	100·03	99·94	100·03	100·17	100·18	100·15	100·61	Total.
$CaCO_3$	54·93	53·12	56·94	53·12	54·68	54·81	54·46	$CaCO_3$
$MgCO_3$	40·36	39·42	38·75	36·99	36·99	38·88	42·57	$MgCO_3$
$FeCO_3$	·64	1·96	1·92	·27	1·28	2·06	1·14	$FeCO_3$
$MnCO_3$	·04	·08	·05	·05	·09	·13	·11	$MnCO_3$
$CaSO_4$	·66	nt. fd.	·40	·21	·26	·31	nt. fd.	$CaSO_4$

* In 597, ·02 per cent. FeS_2 found.
† In 598, ·08 ,, FeS_2 ,,

ANAL. E. G. RADLEY.

ANALYSES OF DOLOMITES.—MONMOUTHSHIRE.

	XXXI.	XXXII.	XXXIII.	XXXIV.	XXXV.	XXXVI.	XXXVII.	XXXVIII.	XXXIX.	XL.	
Lab. No. ...	584	585	586	587	588	589	590	591	592	593	Lab. No.
Slice No. ...	E. 11762	E. 11763	E. 11764	E. 11765	E. 11766	E. 11767	E. 11768	E. 11769	no slice	E. 11761	Slice No.
Insoluble residue	8·95	5·88	4·35	·34	·41	·39	1·10	4·91	14·16	·46	Insoluble residue.
SiO_2 ...	·66	·65	·09	·01	·04	·02	·04	·18	·55	·08	SiO_2
Al_2O_3 ...	2·65	1·82	·91	1·32	1·18	1·05	1·18	1·77	·34	·87	Al_2O_3
Fe_2O_3 ...	·06	·18	·10	·04	·20	·02	·28	·05	·19	·18	Fe_2O_3
FeO ...	1·33	·42	·28	·39	·73	·39	·17	·37	1·16	·65	FeO
MnO ...	·08	·04	·05	·02	·02	·04	·05	·09	·07	·05	MnO
CaO ...	27·86	29·38	29·69	31·23	31·53	31·92	30·81	29·18	26·13	29·79	CaO
MgO ...	16·23	18·05	19·42	19·96	19·17	19·27	19·64	18·88	16·85	20·89	MgO
H_2O at 105° C	·19	·12	·15	·07	·08	·06	·11	·11	·29	·08	H_2O at 105° C.
H_2O above ,,	·65	·47	·57	·37	·42	·44	·58	·55	·61	·44	H_2O above ,,
SO_3 ...	nt. fd.	nt. fd.	·36	·22	·20	·25	·46	·22	·54	nt. fd.	SO_3
C	1·01	·02	·09	·02	·05	·03	·04	·08	·06	·08	C
CO_2 ...	40·46	43·04	44·50	46·45	46·04	46·21	45·59	43·66	39·34	46·61	CO_2
Total	100·13	100·07	100·56	100·44	100·07	100·09	100·05	100·05	100·29	100·18	Total
$CaCO_3$ ...	49·75	52·47	52·55	55·50	56·06	56·68	54·64	51·84	45·95	53·20	$CaCO_3$
$MgCO_3$ ...	33·93	37·72	40·59	41·73	40·07	40·27	41·05	39·46	35·22	43·66	$MgCO_3$
$FeCO_3$ ...	2·15	·68	·45	·64	1·19	·64	·27	·59	1·87	1·05	$FeCO_3$
$MnCO_3$ ...	·13	·06	·08	·03	·03	·06	·08	·14	·11	·08	$MnCO_3$
$CaSO_4$ ...	nt. fd.	nt. fd.	·63	·37	·34	·43	·78	·37	·94	nt. fd.	$CaSO_4$

ANAL. E. G. RADLEY.

XXIV.—Carboniferous Dolomite. Gagg's Quarry, Drybrook, Glos. 1 inch map 233.

XXV.—Carboniferous Dolomite. David Adams' Quarry, Staple Edge, Forest of Dean, Glos. 1 inch map 233.

XXVI.—Carboniferous Dolomite "Red Stone." S. Wales Red Stone Quarry, Mitcheldean, Glos. 1 inch map 233.

XXVII.—Dolomite. Tuft's Level, N.W. of Lydney, Glos. 1 inch map 233.

XXVIII.—Dolomite-mudstone of the "Lid" (base of Whitehead Limestone), from N. road, upper level, New Dun Pit Iron Mine, Glos. 1 inch map 233.

XXIX.—Dolomite from the end of the level heading (Lower Dolomites of the Main Limestone). Tuft's Level, N.W. of Lydney, Glos. 1 inch map 233.

XXX.—Crinoidal Dolomite from the lowest beds of the "Crease." Main Limestone. The highest beds exposed in the quarry (23rd Feb., 1918). Shakemantle Quarry, near Ruspidge, Glos. 1 inch map 233.

XXXI.—Carboniferous Dolomite. Bed No. 1 ... ...
XXXII.— ,, ,, ,, 2 ... ...
XXXIII.— ,, ,, ,, 3 ... ...
XXXIV.— ,, ,, ,, 4 (near base)
XXXV.— ,, ,, ,, 4 (at top) ...
XXXVI.— ,, ,, ,, 5 ... ...
XXXVII.— ,, ,, ,, 6 ... ...
XXXVIII.— ,, ,, ,, 7 ... ...
XXXIX.— ,, ,, lowest, not worked
XL.— ,, ,, Old Quarry. Bed No. 1

} Machen Quarry, Machen, Monmouthshire. 1 inch map 249.

Analyses of Dolomites, Monmouthshire and South Wales.

	XLI.	XLVI.*	XLII.	XLIII.	XLIV.	XLV.
Lab. No.	581	11	595	577	578	580
Slice No.	E. 11760	E. 2314	E. 11759	E. 11757	E. 11758	E. 11754
Insoluble residue ...	·85	·99	·78	1·12	1·58	·22
SiO_2	·17	·11	·10	·36	·06	·04
Al_2O_3	1·41	·25	·65	1·65	1·38	·74
Fe_2O_3	·06	·33	·02	·05	·34	·54
FeO	·51	1·03	1·19	·79	·85	1·39
MnO	·03	·34	·03	·05	·03	·06
CaO	30·70	29·91	32·05	31·46	30·78	30·99
MgO	19·53	20·56	18·54	18·67	18·99	19·35
H_2O at 105° C. ...	·09	·10	·10	·15	·09	·10
H_2O above ,, ...	·60	1·01	·47	·65	·50	·48
SO_3	nt. fd.	—	·23	nt. fd.	nt. fd.	nt. fd.
C	·35	—	·07	·01	·05	·07
CO_2	45·74	45·64	46·01	45·07	45·41	46·33
Total	100·04	100·27	100·24	100·03	100·06	100·31
$CaCO_3$	54·82	—	56·94	56·18	54·96	55·34
$MgCO_3$	40·83	—	38·75	39·02	39·69	40·45
$FeCO_3$	·82	—	1·92	1·28	1·37	2·24
$MnCO_3$	·04	—	·05	·08	·04	·09
$CaSO_4$	nt. fd.	—	·40	nt. fd.	nt. fd.	nt. fd.
	Anal.	E. G. Radley.				

XLI.—Carboniferous Dolomite. Graig Quarry, near Risca, Mon. 1 inch map 249.

XLVI.—Dolomitised Oolite. Oolite Quarry, old tram road, 200 yards E. of last Oolite Quarry, Pwll-du, Mon. 1 inch map 232. *Analyst—Dr. W. Pollard. See Memoir, Sheet 232, p. 35.

XLII.—Carboniferous Dolomite. Castell Coch Quarry, Taff's Well, Glamorgan. 1 inch map 249.

XLIII.—Carboniferous Dolomite. Cwm Quarry, Clydach, E. side, Abergavenny, Brecon. 1 inch map 232.

XLIV.—Carboniferous Dolomite, by waterfall. Bed No. 1. Same locality as XLIII.

XLV.—Carboniferous Dolomite, 15 yards E. of photographed section, Llanelly Quarry, Clydach, Abergavenny, Brecon. 1 inch map 232.

ANALYSES OF DOLOMITES.—SCOTLAND.

	XLVII.	XLVIII.	XLIX.	L.	LI.	LII.	LIII.	
Lab. No.	9	3	4	8	29	1	2	Lab. No.
Slice No.	S. 8129	S. 8130	S. 8131	S. 8132	S. 8283	S. 8063	S. 8064	Slice No.
Insoluble residue ...	1·83	2·42	15·81	28·96	2·01	2·26	1·72	Insoluble residue
SiO_2	·16	·11	·29	·49	trace	·50		SiO_2
Al_2O_3	·21	·28	·36	·50	·10	·45	·34	Al_2O_3
Fe_2O_3				·29				Fe_2O_3
FeO		·34	·32	1·52	·35			FeO
MnO	·17	·24	·19	·33	trace	·22	·19	MnO
CaO	29·65	30·05	25·40	21·73	30·09	30·50	30·53	CaO
MgO	21·53	20·25	18·24	13·61	20·83	21·19	20·81	MgO
P_2O_5	trace ?	trace	·05	·62	trace	—	—	P_2O_5
H_2O	—	—	—	·79	·28	—	—	H_2O
CO_2	46·62	46·15	39·65	31·45	46·59	44·54	46·25	CO_2
Total	100·17	99·84	100·31	100·29	100·25	99·66	99·84	Total

ANAL. DR. W. POLLARD.

XLVII.—Cambrian Dolomite. Quarry, 150 yards E. of Sango Bay, Durness, Sutherland. 1 inch map 114.

XLVIII.—Eilean Hoan, 2½ miles E. of Durness. 1 inch map 114.

XLIX.—Eilean Dubh Group, Eilean Hoan. 1 inch map 114.

L.—Dolomitic Limestone in Fucoid Shales, near Grindaidh, Kyle of Durness.

LI.—Eilean Dubh Group, A'Ghoil Sgein, near Eilean Hoan.

LII.—600 yards N. of Suardal Farm, Skye. 1 inch map 71.

LIII.—625 yards N.W. of Loch Lonachan, Skye. 1 inch map 71.
See 'Summary of Progress' 1898, pp. 197 to 201.
Also 'Tertiary Igneous Rocks of Skye,' p. 146.

Trade Analyses of Dolomites.

	LV.	LVI.	LVII.	LVIII.	LIX.
Calcium Carbonate	52·0	52·5	52·8	54·89	55·37
Magnesium Carbonate	45·2	44·7	44·4	42·07	41·71
Protoxide of Iron ...	—	—	—	·49	·73
Peroxide of Iron ...	—	—	—	·24	—
Oxide of Iron and Earthy matter.	2·0	2·1	2·1	—	—
Protoxide of Manganese.	—	—	—	trace	1·68
Silica	—	—	—	·56	·92
Water	—	—	—	·51	·45
Moisture	·8	·7	·7	—	—
Total	100·0	100·0	100·0	98·76	100·86

LV.—Dolomite. North Anston, Yorks. Upper bed. Anal.—R. Phillips, F.R.S.

LVI.—Dolomite. North Anston, Yorks. Fourth Bed. Anal.—R. Phillips, F.R.S.

LVII.—Dolomite. North Anston, Yorks. Lower or Eighth Bed. Anal.—R. Phillips, F.R.S.

LVIII.—Dolomite. North Anston, Yorks. Anal.—Ransome and Cooper.

LIX.—Dolomite. North Anston, Yorks. Anal.—Ransome and Cooper.

See 'Summary of Progress,' 1901, p. 83.

	LX.
Silica	·43
Lime	55·67
Magnesia	38·62
Ferric Oxide	·50
Alumina	1·50
Carbonic Acid	·97
Combined Water, &c.	2·31
Total	100·00

LX.—Warmsworth Cliff Quarries, Yorkshire. Analysis of the 'lime' made from the stone, as published by the firm.

	LXI.	LXII.	LXIII.	LXIV.
Calcium Carbonate ...	57·366	57·67	53·317	58·02
Magnesium Carbonate	41·145	41·47	40·54	38·33
Silica	·785	·36	·34	·35
Peroxide of Iron ...	·302	·41	}	—
Alumina	·050	·09	} ·78	·12
Iron Oxide	—	—	}	·13
Moisture	·212	—	4·98	—
Sulphur	—	—	·033	—
Phosphorus	—	—	·003	—
By difference	·140	—	—	—
Total	100·00	100·00	99·993	96·98

LXI.—The top Dolomite, 30 feet from top, from Beardwell's Post, Raisby Hill Quarries, Coxhoe, Co. Durham. Anal. F. J. Somerville; Liverpool (Sept., 1913).

LXII.—Sample of Dolomite with smooth fracture, used for basic material. Same locality. (Phosphoric acid ·003 per cent.). Anal. W. F. Keating Stock, Darlington (Nov. 16th, 1903).

LXIII.—Dolomite, Bishop Middleham Quarry, near Ferryhill, Co. Durham. Analysed by the Normanby Iron Works (April, 1916).

LXIV.—Yellow, highly fossiliferous limestone. Fox Cover Quarry, Seaham Harbour. (D. Woolacott, Proc. Univ. Durham Phil. Soc. Vol. IV. part 5, 1912, p. 264.)

LXV.—

Silica	·18 to ·25
Ferrous oxide ... ... }	
Ferric oxide ... ... }	·59 to ·78
Alumina ... ... }	
Lime	30·16 to 31·78
Magnesia	20·91 to 21·73

The average of the whole series (nine samples) is as follows:—

Silica	·22
Iron and Alumina	·63
Lime	30·65
Magnesia	21·33
Carbonic Acid, &c.	47·17
Total	100·00

LXV.—Analyses of samples of Dolomite, Harboro' Rocks, Brassington, Derbyshire, by Dr. H. Louis, 4, Osborne Terrace, Newcastle-on-Tyne.

	LXVI.	LXVII.	LXVIII.	LXIX.	LXX.	LXXI.
Silica	·30	·23	·13	·20	·13	·13
Lime	33·00	34·00	33·40	33·00	32·80	32·80
Magnesia ...	19·67	17·87	19·53	19·74	17·79	21·11

LXVI.—Dolomite. Whitehaven Quarry, Porthywaen. Whitehaven Stinker.

LXVII.—Dolomite. Whitehaven Quarry, Porthywaen. Whitehaven No. 1 (40 inch).

LXVIII.—Dolomite. Whitehaven Quarry, Porthywaen. Upper Gullet No. 2 (Red Bed).

LXIX.—Dolomite. Whitehaven Quarry, Porthywaen. Upper Gullet No. 3 (Buggeroo).

LXX.—Dolomite. Whitehaven Quarry, Porthywaen. Lower Gullet No. 2.

LXXI.—Dolomite. Whitehaven Quarry, Porthywaen. Lower Gullet No. 3.

Anal. Charles E. Tucker, F.I.C., F.C.S.

	LXXII.	LXXIII.	LXXIV.	LXXV.
CaO	30·72	31·12	53·25	29·05
MgO	19·97	19·35	41·75	22·77
SiO_2	1·34	2·44	—	—
Fe_2O_3	·24	·29	·45	·25
Al_2O_3	2·65	1·20	·56	·30
Mn_3O_4	—	—	none	none
SO_3	—	—	·15	·08
P_2O_5	—	—	·01	·01
Siliceous matter ...	—	—	3·83	2·09
Loss on ignition ...	45·28	45·71	—	45·45
Total	100·20	100·11	100·00	100·00
Silica in siliceous matter	—	—	3·10	1·69
Loss on ignition, on sample as received.	—	—	45·45	—

LXXII. and LXXIII.—Raw Dolomite. Dalnatrat, Duror, Argyllshire. Analyses communicated by Messrs. Stewarts & Lloyds, Steel Works, Mossend, Holytown, Lanarkshire.

LXXIV.—Average sample of Duror Dolomite (Ignited). Analyses by Messrs. Wallace & Clark, Glasgow.

LXXV.—Average sample of Duror Dolomite (Raw Dolomite calculated from figures in LXXIV). Analyses by Messrs. Wallace & Clark, Glasgow.

CHAPTER X.

Methods Adopted for the Analysis of Dolomites.

An average sample of each of the dolomites collected by officers of the Survey from the various quarries was broken up to pass a sieve of 30 holes to the linear inch. This was thoroughly mixed and quartered until a sample of about 50 grammes was obtained. The portion thus prepared was ground in an agate mortar so as to pass a sieve of 60 holes to the linear inch. No advantage was found in grinding the material to a finer state of division, and the 60-hole powder was used for all the estimations.

After each sampling the sieves were carefully brushed, and small portions of the rock next to be broken up were first ground and sieved in successive stages, these portions being rejected. A further brushing completed the preparation of the sieves for the subsequent sample.

All estimations were made in duplicate, this being the only complete check upon the accuracy of the analyses. If the duplicates did not agree within narrow limits, viz., 0·06 per cent. on the CO_2 and 0·04 per cent. on SiO_2 and 'insoluble residue,' etc., further duplicates were made.

Some trouble was experienced in obtaining comparable results in the estimation of some of the constituents of the dolomites, even after several duplicates had been made. Items such as 'insoluble residue' have no meaning unless the actual method of analysis is stated. Similarly, the term 'loss on ignition' conveys a wrong impression.

Such being the case, it became necessary to adopt certain definite methods of analysis. Those that were adopted and the reasons for their adoption are discussed in the following pages.

Insoluble Residue.

It will be noticed that 'insoluble residue' has always been determined. Other workers do not usually estimate this, but it was believed that some information as to the composition of the detrital minerals would help in elucidating points which had not been investigated. Silica and alumina etc., in the colloid state, were almost invariably present, and probably originally existed in the rocks as clays or other aluminous minerals. As these two compounds were not completely dissolved, even after long-continued boiling and prolonged digestion with acid on a water-bath, a certain definite time for boiling, etc., was taken. Duplicates made in the same manner gave results which were comparable, while if one duplicate was treated in the usual way it produced one result, and the other, if boiled twice as long, showed, where the percentage of insoluble residue was high, a difference of nearly 2 per cent. The strength of the acid employed also has an effect upon the result, some of the constituents being to a

greater extent carried into solution by a more concentrated acid than that usually employed. The insoluble residues of Lab. Nos. 596 to 599 were deeply stained with iron oxide. As it would take about two days' digestion to dissolve all the iron left in these residues, the same routine was followed in these cases as with the remainder of the series, for the sake of comparison.

The results given were obtained in the following manner:—

Five grammes of the rock-powder were placed in a covered beaker and an excess of dilute hydrochloric acid (1 volume chem. pure HCl of S.G. 1·16 to 3 volumes of H_2O), very carefully added so as not to lose any of the material by spurting. When the violence of the action had diminished, the beaker was placed upon a water-bath for about half-an-hour. All apparent effervescence having ceased by that time, the liquid was boiled for five minutes to ensure complete solution of the carbonates.

The solution was filtered and the residue washed with hot water until no chloride was left, ignited over a bunsen-burner for about one hour, and the ignition completed by heating with a blowpipe for five minutes.

After cooling in a desiccator and weighing, the residue was re-heated for a further five minutes. A difference of more than 0·2 milligramme between the first and second weighings was rare. The result represented what is called 'insoluble residue.'

Silica.

The filtrate obtained in the preparation of the insoluble residue was transferred to a dish and concentrated on a water-bath to as near dryness as possible, then heated carefully to ensure dehydration of the silica. An excess of hydrochloric acid retards the operation, owing to a higher temperature being required to volatilise this compound. The chlorides of calcium and magnesium, being exceedingly hygroscopic, also prevent rapid dehydration of the silica.

When cold, the residue was moistened with HCl and water, filtered, washed thoroughly and then ignited, the operation being finished with the blow-pipe.

A constant weight having been obtained, dilute sulphuric acid and hydrofluoric acid were added and the mixture carefully heated to dryness and ignited. The residue, consisting of iron and aluminium oxides, was deducted from the total weight of 'silica' found.

Iron and Aluminium Oxides.

The filtrate from the silica was oxidised by a few drops of concentrated nitric acid, boiled, just neutralised with ammonia, and, while boiling, a hot solution of ammonium acetate added, thus separating the iron and aluminium as basic acetates from the manganese-, calcium- and magnesium compounds. The precipitate was filtered off, washed with hot water, re-dissolved in HCl, re-precipitated by ammonia, and washed thoroughly with hot water.

In no case was any lime or magnesia found to be precipitated along with the hydrated iron and aluminium oxides.

The combined filtrates were concentrated to a small bulk and the small quantity of iron-alumina which had passed into solution was precipitated, filtered, and added to the main portion.

The flocculent hydrated oxides of iron and aluminium were dried in a steam-oven and separated as completely as possible from the filter-papers. These papers were first ignited in the crucible containing the residue from the 'silica,' the dried precipitate was then added and the whole strongly ignited and weighed.

To dissolve the mixture of iron and aluminium oxides, acid potassium sulphate was introduced and the whole fused very slowly.

After allowing the crucible to cool, it was immersed in water containing dilute sulphuric acid and warmed to dissolve the mass.

Occasionally the precipitate was found to contain a small quantity of silica which was dealt with as before, and its weight deducted from that of the Fe-Al oxides.

The iron and aluminium having been obtained in solution, sulphuretted hydrogen gas was introduced into the hot liquid, and any platinum which had been derived from the crucible was thrown down and filtered off, the liquid transferred to a flask fitted with a cork and two tubes, and sulphuretted hydrogen passed through the boiling liquid for about five minutes to ensure total reduction of the iron to the ferrous state.

In order to expel the dissolved sulphuretted hydrogen, a stream of carbon dioxide was employed, the solution being kept boiling until all traces of H_2S had been removed. The contents of the flask were then cooled as rapidly as possible.

When cold the Fe-Al solution was titrated with potassium permanganate and the result calculated as Fe_2O_3, which represents the total percentage of iron, whether present as Fe_2O_3, FeO or FeS_2; the last two items, estimated and calculated as Fe_2O_3 are deducted from the total percentage of Fe_2O_3.

After the total amount of Fe_2O_3 had been subtracted from the weight of Fe-Al precipitate, the residue was taken as the percentage of alumina present in the rock.

Attempts were made to estimate directly the percentage of alumina as such, but it was found that no advantage was gained by this procedure.

P_2O_5 and TiO_2 were looked for in a solution prepared in a similar manner to the above, but were not found. If present, their percentage would have to be deducted from the Fe-Al precipitate, otherwise that would be included in the alumina.

Manganese.

The concentrated filtrate from the iron-aluminium precipitate was placed in a flask, sulphuretted hydrogen introduced, the flask corked and allowed to stand. As such a large quantity of calcium and magnesium salts were known to be present, it was thought advisable to re-precipitate the manganese sulphide, to ensure freedom from those two compounds. The manganese sulphide was then filtered off, washed with a dilute solution of ammonium sulphide, dissolved in dilute hydrochloric acid and concentrated to dryness on a water-bath. Sodium carbonate was added to

destroy ammoniacal compounds, and when concentrated once more the manganese was brought into solution by the addition of a few drops of dilute HCl and H_2SO_3. When in solution, the manganese was precipitated by sodium carbonate and boiled. After standing over-night it was filtered and ignited to Mn_3O_4, being finally calculated to MnO.

The possibility of the inclusion of some $CaSO_4$ in the manganese ppt. must not be lost sight of, but although tested for, it was not found in the samples dealt with during the present investigation.

Calcium Oxide.

Five grammes of rock-powder were used for the preceding estimations, but it has been found in practice that the precipitates of calcium and magnesium from one gramme of rock-powder were the greatest that could be thoroughly washed, etc., unless an undue amount of time was expended. Hence, for the determination of these constituents, a further known weight of about one gramme of the rock-powder was weighed out and decomposed by HCl, all compounds other than those of calcium and magnesium being removed. This was thought to be preferable to making up the filtrate from the manganese precipitate to a known volume, say 500 c.c. and then using 100 c.c. of it. The employment of sulphuretted hydrogen as a precipitant of manganese was avoided because the use of that gas might have led to the formation of calcium sulphate, which would not be easily soluble in dilute hydrochloric acid when re-precipitating the calcium oxalate, the small quantity of manganese present being therefore removed along with the Fe-Al ppt. by ammonia.

A solution of calcium and magnesium in HCl having been obtained, it was raised almost to boiling-point, neutralised with ammonia and a hot solution of ammonium oxalate added, thus precipitating the calcium as oxalate. Ammonium oxalate was used in preference to carbonate owing to the greater solubility of calcium carbonate and also to the increased likelihood of magnesium carbonate being simultaneously precipitated.

After the solution had stood for some hours on a hot-plate, the precipitate was filtered off, re-dissolved in dilute HCl, and re-precipitated as oxalate. A second precipitation is essential, small quantities of magnesia being frequently carried down mechanically by the calcium oxalate. The filter-papers were ashed, digested with HCl, and the liquid added to the solution before the second precipitation, small amounts of calcium salts being sometimes retained by the paper.

Having been filtered off and thoroughly washed, the calcium oxalate was ignited in a platinum crucible, at first very slowly, finally completing the operation with a blow-pipe, thus converting the oxalate into oxide. It was then cooled and weighed.

It has long been known in the Survey laboratory that this ignited precipitate does not truly represent the percentage of CaO in the rock in question, but consists of a mixture of CaO and $CaSO_4$ in indefinite proportions.

When pure calcium carbonate is heated for some time by a blow-pipe, CO_2 is driven off and CaO remains. The weight of

lime as found always differs from the weight that is required theoretically. It was demonstrated that all carbon dioxide had been expelled, but tests revealed the presence of sulphate, the sulphur having been derived from the gas used in the ignition.

Actual experiments have shown that the quantity of sulphur absorbed is largely dependent upon the time occupied in the operation of ignition, also on the quantity of material involved and whether the mass is in a heap or is thinly spread. Apparently the $CaSO_4$ first formed tends to hinder the conversion of the whole mass into sulphate under ordinary conditions. Attempts were made to see how long it would take to bring about this change, but after 12 hours heating over a bunsen-burner, with a final 15 minutes with a blow-pipe, there still remained a considerable amount of CaO unchanged.

The figures given below record the results of these experiments.

Pure calcium carbonate heated for about one hour, with a final 5 minutes over a blow-pipe, cooled, weighed, and then re-heated for a further 5 minutes by the blow-pipe, etc. Variation between first and second weighings, 0·0006 gramme on 1·0021 gramme. The other samples varied from 0·0002 to 0·0005 gramme under the same conditions.

	$CaCO_3$	CaO calc.	CaO found.	Diff.
Thinly spread	·5662	·3170	·3260	·0090
Heaped up	·8653	·4845	·4882	·0037
Thinly spread	1·0006	·5603	·5655	·0052
Heaped up	1·0021	·5611	·5652	·0041

The crucible containing the 1·0021 grammes of calcium carbonate when heated for 12 hours at intervals of 3 hours, with a final 15 minutes with a blow-pipe, gave the following results:—At 3 hours, 0·5794; at 6 hours, 0·5847; at 9 hours, 0·5883; and at 12 hours, 0·5886 gramme of 'CaO.' After conversion into calcium sulphate by the addition of sulphuric acid, theoretical values were obtained for the calcium oxide present.

To meet this difficulty we have adopted the plan of converting the CaO into $CaSO_4$ by the addition of dilute H_2SO_4, and then calculating the percentage of CaO from the sulphate so prepared. Great care is essential when driving off the excess of acid by heat, to avoid loss by 'creeping' or spurting.

After weighing, the $CaSO_4$ was tested for magnesia, and, where necessary, corrections were applied, but in no case was any great quantity found.

Magnesium Oxide.

In some cases the combined filtrates from the calcium oxalate precipitates were concentrated to dryness and then gently heated to expel ammonium salts, the presence of which is supposed to prevent the precipitation of magnesium compounds. In other cases the filtrates were concentrated to volumes of 400 c.c., made alkaline with ammonia, and then microcosmic salt was added. No advantage was obtained by destroying the excess of ammonium salts before precipitation, provided that at least 24 hours were

allowed to elapse before filtering off the magnesium precipitate. The procedure was as follows:—

The solution having been concentrated to about 400 c.c., it was allowed to cool, then made just alkaline with ammonia and a solution of microcosmic salt (1 to 10) added, a little at a time. Between each addition of a few drops, the solution was thoroughly stirred and allowed to stand for about 5 minutes. When the requisite quantity of microcosmic salt had been added, the solution was set aside for at least 24 hours, then filtered and washed with dilute ammonia. A second precipitation is essential, owing to the probability of other salts being included in the first precipitate. When carried out in this manner, the precipitation of the magnesium is almost invariably complete.

The magnesium precipitate having been washed, it was dried in a steam-oven and detached as completely as possible from the filter-paper. The paper was ignited in a porcelain crucible and the salt was then added to its residue, and the whole strongly ignited over a bunsen-burner.

This procedure was found to be preferable to igniting the filter-paper and salt together, as the ignition did not take so long. When ignited together with the precipitate, the carbon from the filter-paper required a much longer time to burn off.

The magnesium pyrophosphate when prepared in this manner, must not be assumed to be pure at this stage, for small quantities of silica and alumina, etc., are frequently present (probably derived from the dishes and beakers used), and these must be deducted from the magnesia found. Similarly, the traces of lime which almost always have escaped precipitation must be looked for, and when found, the weight subtracted from the magnesia. For other sources of error, see Bulletin 422 of the U.S. Geol. Survey, pp. 123-128.

Water.

The water existing in rocks usually occurs in two forms, that present in the hygroscopic state, which is determined by heating from 100° to 105° C., and that which comes off when the rock is heated to redness after drying at those temperatures.

Hygroscopic water was determined by heating the rock-powder contained in a platinum 'boat' in a toluene-bath which gave a steady temperature of 105° C. for about 2 hours. Very rarely was a difference found if heated for a further period.

The water 'above 105° C.' was estimated, by transferring the 'boat' and powder used for the above experiment to a glass tube heated by a gas-furnace, and absorbing the water evolved in a U-tube filled with fragments of pumice which had been saturated with concentrated sulphuric acid. A portion of the glass tube was filled with pumice, coated with lead peroxide to absorb any sulphur dioxide which might be formed. A current of dried air was passed through the tube while the operation was in progress in order to drive the moisture into the U-tube. When all the water had been absorbed, the tube was cooled and the difference in its weight, before and after the experiment, gave the percentage of water present.

Carbon Dioxide.

The usual method of estimating CO_2 is by decomposing the rock with dilute HCl and determining the loss in weight.

For the purposes of this investigation, the CO_2 evolved by the action of dilute HCl (one part HCl of S.G. 1·16 to 4 parts of H_2O) on the carbonates, was absorbed in caustic potash, and the increase in weight represented the percentage of carbon dioxide in the rock.

A weighed quantity of rock-powder was put into a flask fitted with a rubber stopper through which passed two tubes, one to admit dilute HCl contained in a small flask, the other being the internal tube of a reflux condenser. To the upper end of the condenser tube was fitted a U-tube containing pumice drenched with concentrated sulphuric acid to dry the gas evolved, this in turn being connected to two Geissler potash-bulbs which were about half full of potash, to absorb the CO_2 liberated. As moisture is always driven off from the solution of potash and would, unless caught, occasion a loss, a further desiccating U-tube was attached to the bulbs. A steady stream of air, freed from CO_2, was drawn through the apparatus by a pump, and in this manner the dilute HCl was syphoned from the small flask and allowed to act upon the rock, CO_2 being liberated and drawn into the potash-bulbs, there to be absorbed.

When all apparent action had ceased, the liquid was boiled and the CO_2 in solution thus expelled. The boiling was continued for 5 minutes, the current of air driving all traces of CO_2 into the potash-bulbs.

To ensure that all CO_2 had been drawn from the flask and condenser-tube, the passage of air through the apparatus was continued for from a half to one hour.

The method given is only applicable when the absence of sulphides which are easily decomposed by dilute acids has been confirmed. Some dolomites and limestones contain zinc-blende, etc., which, when treated with acids, give off H_2S, and this would be absorbed in the potash and weighed as CO_2.

If the presence of a decomposable sulphide has been proved, a slightly different procedure must be adopted. In the place of the sulphuric-acid tubes, calcium chloride must be used to absorb water, and soda-lime for the CO_2, while before passing through these tubes, the gas must be freed from H_2S by the addition of a U-tube filled with anhydrous copper sulphate. The method is fully described in Bulletin 422 of the U.S. Geol. Survey.

Carbon.

As the percentage of carbon in a dolomite is nearly always small, 5 grammes of the rock-powder were treated with dilute HCl and the solution filtered through purified asbestos, which was then dried. The asbestos and residue were transferred to a platinum 'boat,' placed in a tube, as for water-estimation, and heated. A current of CO_2 free air was passed through the tube and the resulting CO_2 absorbed in the potash-bulbs as used in the estimation of carbon dioxide.

Sulphur Trioxide.

To determine the percentage of this constituent, a weighed quantity of the rock-powder was put into a flask provided with a cork and two tubes, through which a current of CO_2 could be passed. Dilute HCl of the same strength as that used for CO_2 was introduced, and the mixture carefully boiled after all effervescence had ceased. The boiling was continued for about 15 minutes, experiments proving that all sulphur in the state of sulphate had passed into solution during that time, while leaving any FeS_2 unchanged. The solution was then filtered, washed, made hot, and, while hot, barium chloride was added to precipitate the sulphur as $BaSO_4$.

It was found necessary to have a stream of CO_2 passing through the liquid continuously, owing to the risk of pyrites, if any, being oxidised by admission of air, thereby setting free the sulphur, which would of necessity be estimated as sulphate.

That the sulphate existed only as calcium sulphate and not as magnesium or other soluble sulphates was proved by boiling a portion of the rock-powder with water. Only small quantities of $CaSO_4$ were found in the filtered solution, but the possibility of the presence of magnesium sulphate must not be lost sight of, notable amounts of that salt having been found in weathered samples of dolomites, especially after having formed part of buildings in towns.[1]

The possibility of the presence of the more insoluble sulphates such as those of barium and strontium must not be forgotten. If present, the amount of SO_3 found would probably be too low, but in the specimens under examination neither of these two compounds was detected.

Ferrous Oxide.

In the dolomites analysed for this investigation, the ferrous oxide existed as ferrous carbonate.

A weighed quantity of the rock-powder was decomposed by dilute sulphuric acid (1 part of concentrated acid to 5 parts of water), in a manner similar to that adopted for the estimation of SO_3. After boiling for about 10 minutes, the solution was cooled as rapidly as possible to the temperature of the laboratory and titrated with potassium permanganate.

That the FeO found was present as $FeCO_3$ and not as any other mineral, such as magnetite, was shown by dissolving the rock-powder in HF and H_2SO_4 in a current of CO_2. The results proved to be comparable. Magnetite, when treated under the same conditions as those used for the dolomites, was found to be insoluble.

The small quantity of carbon present in the rocks was insufficient to have any marked effect upon the results. When carbon

[1] 'Summary of Progress of the Geological Survey of the United Kingdom for 1901,' pp. 83 to 86.

in the proportion found was mixed with pure ferrous ammonium sulphate, and treated by the method described, theoretical values for FeO were obtained. There is no doubt that with larger quantities of carbon and less dilute acid, incorrect results would be obtained, owing to the reduction of the Fe_2O_3.

Pyrites.

In only two of the dolomites under discussion was pyrites found. This constituent may have originally been present in others, during the course of time becoming converted into Fe_2O_3, the liberated sulphur on oxidation forming gypsum with some of the calcium carbonate. It was estimated in this manner:—

Two grammes of the rock-powder were fused with 10 grammes of sodium carbonate and 1 gramme of potassium nitrate. The melt was allowed to cool, leached with water, and the resulting filtrate acidified with HCl. The solution was then boiled and $BaCl_2$ solution added. The $BaSO_4$ so formed was filtered off and ignited. The result gave the total percentage of sulphur present in the rock, and when that portion which was due to sulphate had been deducted, represented the sulphur existing as pyrites. Blank experiments were carried out, and corrections for sulphur introduced from the gas applied.

Phosphate.

In some dolomites, P_2O_5 has been observed. This constituent was tested for, but not found in the present samples, either in the insoluble residue or in the soluble portion.

Loss on Ignition.

In many analyses of dolomites and other rocks, the percentage 'loss on ignition' is given.

Theoretically, this should indicate the total percentages of the constituents of a rock which are capable of being volatilized by heat; and in the cases of dolomites and limestones, would include CO_2, C, H_2O, and any combustible sulphur in the form of pyrites, etc. In practice, however, a considerable difference will be noticed between this 'loss' and the total percentages of the constituents when determined directly.

Estimations of the 'loss on ignition' of each of the dolomites analysed, were made, with varying results.

About 1 gramme of the rock-powder was placed in a covered platinum-crucible and heated for 1 hour, receiving at the last, 5 minutes' ignition over a blow-pipe. This was repeated until the weight was constant.

It was found that the heating should be very gradual at first as the greater part of the CO_2 comes off rapidly, small quantities of the powder being thus frequently lost by spurting and included in the 'loss on ignition.' In many cases, however, the percentage of 'loss' was not so great as the percentages of volatile constituents, and in only two instances did the theoretical and practical results agree.

There are many factors which might have an effect upon the estimation of the 'loss on ignition.' As previously stated, the risk of mechanical loss of the rock-powder is great. Similarly, the oxidation of sulphides would affect the result.

Where the theoretical does not correspond to the observed loss the difference may be ascribed, amongst others, to the following causes:—

1. Incomplete ignition. Although the final weights were constant, in three cases small quantities of CO_2 remained.

2. Admission of sulphur from the gas employed, as described under the estimation of CaO. When ignited for a short time, the rock-powders gained in weight between the first and second ignitions. As long-continued heating is necessary to get constant results, the small quantity of carbon present is insufficient to reduce the sulphate as rapidly as it is formed, and is probably destroyed before the formation of the sulphate.

3. Oxidation of ferrous carbonate to ferric oxide. This would, if the percentage of FeO was high, and the FeO completely oxidised, modify the 'loss on ignition' to a considerable extent.

For further remarks upon this subject, *see* Bulletin 422 of the U.S. Geol. Survey, pp. 231-232.

CHAPTER XI.

Treatment and Uses of Dolomite.

Calcination.

Dolomite carefully selected with reference to its content of silica and alumina is converted into what is known as 'shrunk dolomite' by a process of calcination at a high temperature in specially-constructed kilns. Shrunk dolomite is mainly employed as a basic lining to converters and for the hearth and banks of the open-hearth basic furnace.

On calcination, dolomite undergoes a progressive dissociation which may be considered chemically as covering two distinct stages. The first effect of rising temperature is the expulsion of carbon dioxide from the magnesium carbonate contained in the dolomite and the formation of a mixture of magnesium oxide and calcium carbonate, accompanied by a considerable reduction in volume. During this stage, in all probability, a combination will be effected between the impurities of the dolomite, such as silica, alumina, etc., and an equivalent amount of magnesia, resulting in the formation of such compounds as magnesium orthosilicate (*forsterite*), magnesium aluminate (*spinel*), and magnesium aluminium silicate (*pyroxene*). The formation of any or all of such compounds will, of course, be dependent upon the relative amounts of silica and alumina present. Forsterite will form in those rocks in which silica is in excess of the alumina, while spinel is only possible in cases where the alumina is predominant.

Such changes and combinations would be in complete accordance with those proved to have taken place during the metamorphism of dolomitic rocks by natural agencies.

Complete calcination results in the expulsion of the remaining carbon dioxide, a still further reduction in volume, and the production of a dense crystalline aggregate of magnesium and calcium oxides.

Microstructure.—Pure dolomite, when fully burnt, consists of a ground-mass of crystalline *lime*, throughout which are scattered very numerous, small, rounded grains of *periclase*. The structure is remarkably compact and the only cavities present represent spaces that existed in the limestone used; the porosity occasioned by the loss of CO_2 has thus been almost completely eliminated by the crystal-growth of the oxides. Both constituents belong to the cubic system and pure burnt dolomite is therefore isotropic. The structure is seen in the fine-textured areas in Fig. 5*b*. Sections of ordinary commercial material nearly always show the presence of two common impurities, namely, excess lime and silica. Excess lime, if due to a general deficiency in the magnesia-content of the stone, is evidenced by a relative scarcity of the the periclase granules, but if, as frequently happens, it is present

as veins or crystals of calcite, these are converted into patches of pure lime which has a coarsely crystalline structure with cubic cleavage. Such a vein is shown in Fig. 5*b*. Silica, which is generally present to the extent of from 2 to 7 per cent., is indicated by weakly birefringent areas that represent lath-shaped crystals of a silicate. This silicate (No. 3 below) is certainly very rich in lime, and a relatively small quantity of silica suffices to convert the whole of the free lime of the dolomite into silicate. Pieces of dolomite rich in silica occasionally pass through the kilns and have a glazed appearance after burning. A section through such a piece is shown in Fig. 5*a*; the free lime has been almost entirely replaced by an aggregate of elongated silicate crystals, while the periclase granules remain scattered throughout the mass. The presence of so much magnesia in the form of periclase must be taken to indicate that under these conditions the silicate does not dissolve any considerable amount of magnesia. These siliceous fragments keep their shape well, and it would appear that the silicate is solid at kiln temperatures.

a. *b.*

FIG. 5.—Microstructure of Burnt Dolomite.

a.—Glazed Siliceous Burnt Dolomite. The ground-mass is largely composed of lime silicate containing abundant granules of periclase. Numerous lath-shaped crystals of the same compound are visible and include scattered grains of periclase. × 25 diams.

b.—Ordinary Burnt Dolomite. Fine granules of periclase imbedded in crystalline lime. The light area is nearly pure lime and represents a vein of calcite in the original rock. × 25 diams.

Artificial additions of silica are sometimes made with a view to protecting the dolomite from perishing, the object being to produce a glaze upon the surface; in this case the silicate of the glaze may be of a more acid character than that formed in the body of the dolomite. The ortho-silicate, if formed, causes disin-

tegration owing to a sharp volume-change that occurs on cooling, and for this reason the use of silica seems to be inadvisable; some success has been obtained by the addition of iron oxide.[1]

Perished dolomite.—When burnt dolomite is exposed to the action of water, the free lime becomes converted into an aggregate of birefringent flakes of calcium hydroxide; these are sometimes seen in sections that have been ground with water. The mass falls to a powder and is useless for the furnace hearth. In the powder the periclase granules remain unaltered, they are but little soluble even in hydrochloric acid and may be separated by this means. Methods for the isolation of the magnesia have been proposed which depend on similar reactions to the above. On account of the porous texture of the perished dolomite it does not seem possible to restore the original compact structure by re-burning, though the expulsion of the water is easily brought about.

The lining of the dolomite kiln.—The kilns are lined with basic material rammed with tar and burnt in. The function of the tar is very obscure, but it is generally held to be essential for the close fritting of the basic material. Sections through the lining in a partly-burnt and in a completely-burnt condition show that the burning results in a continued growth of the grains of magnesia and of the interstitial lime; the structure remains otherwise very similar to that of the burnt dolomite. It is observed by the manufacturer that fragments of siliceous rock are apt to form slag, and so adhere to the walls of the kiln; conversely, the kiln walls will require to be sufficiently low in silica to remain solid and dry at the furnace temperature.

Use in Furnaces.

In the basic process the banks of the furnace are exposed to the action of a highly basic lime-slag containing up to 50 per cent. of CaO. For this reason the banks must be composed of a highly basic refractory material, of which the constituents only melt at temperatures higher than those that prevail in the furnace; the most suitable material has been found to be burnt dolomite. The conditions in the basic furnace, both as regards temperature and gas, closely resemble those that obtain in the acid furnace, the temperature in both cases being approximately 1,650° C.

A preliminary examination of the System CaO-MgO has been made in the Geophysical Laboratory at Washington, U.S.A. It has been shown that the melting-points of all mixtures of magnesia and lime are very high, that no compounds between these oxides are formed, and that solid solution of one oxide in the other does not occur to any considerable extent. On the solidification of fused mixtures of the oxides lime and periclase crystallise side by side.

Lime forms colourless isotropic crystals with well-defined cubic cleavage and high refractive index (1·83). The melting-point has been estimated to be about 2,570° C., and the specific gravity 3·15.

[1] The effect of various additions on the keeping properties of dolomite has been discussed by G. Schurecht, *Journ. Am. Cer. Soc.*, vol. 2, 1919, p. 291.

Magnesia in the crystalline form of periclase builds colourless isotropic octahedral crystals or rounded grains with cubic cleavage and has a refractive index of 1·734. It melts at a very high temperature and has a specific gravity of 3·674.

Structure of the basic hearth.—The basic hearth, while consisting essentially of the mixed oxides, contains also an appreciable quantity of silica, part of which may have been present in the dolomite used, while the remainder may be derived from slag that has penetrated or that has been purposely added in making the hearth. Considerable amounts of ferrous and ferric iron are also present.

The various constituents give rise to a number of crystalline compounds in addition to lime and periclase.

In Pl. VII, Fig. 2, will be seen a micro-section that illustrates the structure and composition of a dolomite bank at a position near the 'wash.' It is a mosaic of various crystalline compounds, and in considering such a structure it must be borne in mind that the crystals of the chief component minerals have grown at temperatures far below their respective melting-points. For this to occur it is not even necessary for an interstitial melt to be present, for it has been shown by Shepherd, Rankin and Wright that at ordinary atmospheric pressures, and in the dry state, crystals of calcium oxide coalesce and grow rapidly at 1,400° C. The structure so obtained is granular, the size of the component grains increasing with the duration of the heating, and is comparable with that produced in rocks that have been subjected to a high degree of thermal metamorphism but have not been melted. It will be seen that in Fig. 2 there are traces of a coarse aggregate structure, certain elongated crystals being arranged along lines so as to divide the field into several areas containing material of the usual fine rounded grain. The lines are composed of a silicate of lime; they probably follow the outline of the original dolomite-fragments, and it is possible that they represent an infilling of the interstices with a little basic slag. Details of the average structure are shown with higher magnification in Pl. VII, Fig. 1, in which three of the following constituents are seen.

(1) Lime: Large isotropic crystals show very perfect cubic cleavage. Their outline is quite irregular, being in most places that imposed by the shape of the adjoining mineral grains. The size of the crystals indicates rapid grain-growth in the manner mentioned above.

(2) Magnesia: — Periclase. Small yellowish rounded grains are scattered throughout the section; several can be seen adjoining the large crystals of lime, and they are sometimes embedded in this constituent. Samples of the bank when kept in the open air fall to pieces owing to the slaking of the lime. The magnesia, however, does not at first undergo any alteration, and can be isolated by digesting the powder in moderately strong hot hydrochloric acid and removing the gelatinous silica by the addition of a little hydrofluoric acid. The residue forms a yellow powder which on qualitative analysis yielded chiefly magnesia. Manganese and ferrous iron were however present in noticeable

amount. The refractive index was found to be somewhat higher than 1·76, a value distinctly above that for pure periclase. It seems likely therefore that these oxides are present in solid solution.

(3) Tricalcic silicate?—Elongated crystals seen arranged in lines in Fig. 2 are also found in other parts of the section, but do not occur in Fig. 1. When etched with hydrochloric acid their surfaces become covered with a film of gelatinous silica which may be stained easily with organic dyes.

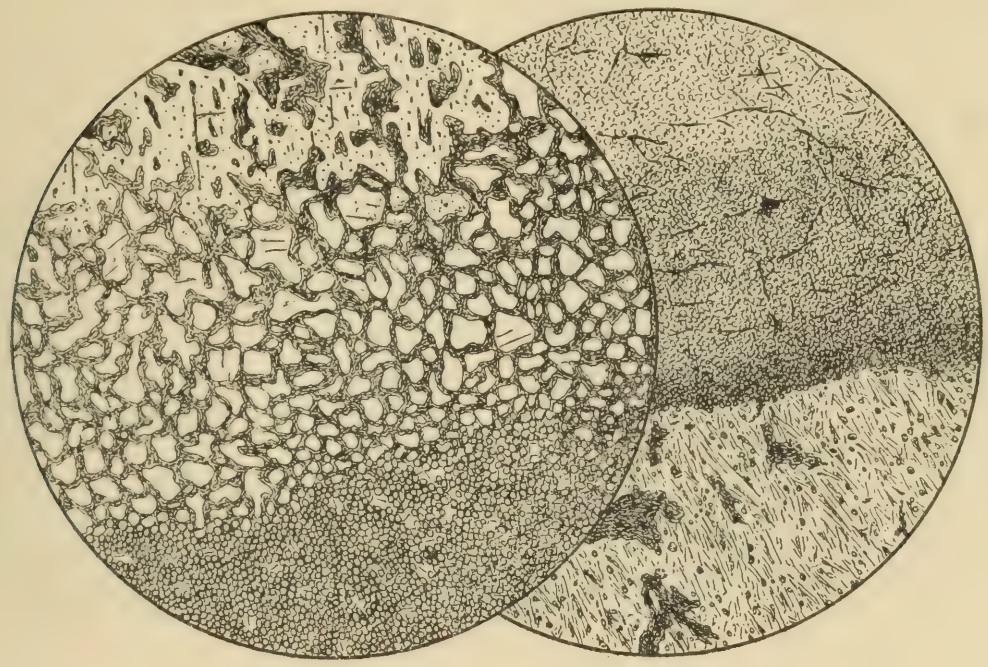
The mineral is weakly birefringent and has a longitudinal cleavage, moderate refractive index and straight extinction. It appears to agree in general character with the tricalcic silicate (F. E. Wright *loc. cit.*), but further investigation will be required before its identity is definitely established.

(4) Magnesium silicate?—The fourth constituent occurs in numerous grains with moderate birefringence. The optical properties are obscured by iron-staining, which occurs to a variable extent, but frequently imparts a deep brown tint to this substance, as in Fig. 1. With hydrochloric acid it is readily decomposed and yields a thick film of gelatinous silica.

The sections described above were taken from the bank of a basic fixed furnace that had only been in operation for three weeks; they exhibit well the structure of a relatively pure dolomite bank at a distance of about 3 inches below the surface. Two samples from a Talbot furnace-hearth will serve to illustrate the conditions at the extreme surface and at a point near the brickwork. The latter sample consists of large fragments of dolomite cemented in a dark slaggy matrix. In thin section the dolomite is seen to be in an almost unaltered condition, but is stained a deep brown at the margins by the penetration of iron from the interstitial slag. (Fig. 6*b*). The periclase is here stained yellow while the lime has been converted into silicate; a certain amount of material has been dissolved and small grains of periclase, which are stained to a rich brown, remain scattered along the margins of the dolomite fragments. The interstitial slag contains well-developed silicate crystals together with an ill-defined brown compound.

The superficial layer of the hearth is deeply stained with ferric iron, and in many places is opaque in thin section, showing only small angular patches of clear white silicate. It must be borne in mind that on account of the constant repairs this layer has not the same age as the inner portion. At a distance of perhaps an inch from the irregular surface the bank is lighter in colour and has a crystalline cleavage. The section (Fig. 6*a*) shows the presence of lime and calcium silicate, together with much periclase The grain-size of the latter is moderate in the centre of the dolomite fragment, but increases rapidly in the outer layers; coalescence is apparently assisted by the removal of the lime as a fluid slag which is expelled from between the grains, for these are only separated by a narrow dark network. The larger grains show a good cubic cleavage. In places grain-growth has become so vigorous that neighbouring grains have joined and assumed parallel orientation over considerable areas, the slag then appearing as small rounded inclusions in a ground-mass of periclase

(Fig. 6*a*). This coalescence leads to the formation of an impervious coating of periclase which will no doubt protect the underlying dolomite from the action of the slag.



a *b*

FIG. 6.—Basic Hearth; Microsections.

a.—Dolomite from the surface of a basic hearth. The lime has been converted into a dark slag, while the periclase has increased in grain-size especially in the upper portion which represents the outside of the dolomite fragment. × 25 diams.

b.—Dolomite from within the bank of a basic furnace. The ordinary fine-grained burnt dolomite is seen to be stained with introduced iron on the outside of the fragment. The lower part of the field shows the interstitial slag, consisting chiefly of lime silicates. × 25 diams.

Stability of the basic hearth.—Lime, magnesia and burnt dolomite are all perfectly infusible at the temperatures reached in the basic hearth; nevertheless, as is well known, it would be impossible to form a satisfactory hearth by the use of lime in place of dolomite. Magnesite hearths, on the other hand, have been used successfully, especially in America. The durability of the material seems to be closely connected with the marked resistance of magnesia to attack by calcium silicate; this property, so strongly evidenced in the preceding descriptions, probably extends to the action between the bank and the slag of the bath itself.

Besides the oxides, the silicates $3CaO.SiO_2$, $2CaO.SiO_2$ and $2MgO.SiO_2$ are solid at temperatures reached in the furnace, but their melting-points are greatly lowered by the addition of impurities. In those parts of the hearth which are not directly in contact with the melt they will be largely in the solid state, and there does not seem to be any special reason for the use of magnesite in preference to dolomite; at the surface, however, there is reason to think that magnesite will be more resistant to the continued attack of silica in the slag. Fettling with a mixture somewhat richer in magnesia may therefore be advantageous, especially if the dolomite is rather rich in lime.

EXPLANATION OF PLATE IV.

Sections of silica-bricks showing variation in the degree conversion of the quartz, both in the ganister and in the ground-mass.

For detailed description *see* page 61.

Fig. 1.—American silica-brick. F. 2446. × 32 diams.

Fig. 2.—British silica-brick, South Wales. E. 11467. × 32 diams.

Fig. 3.—French silica-brick. F. 2445. × 32 diams.

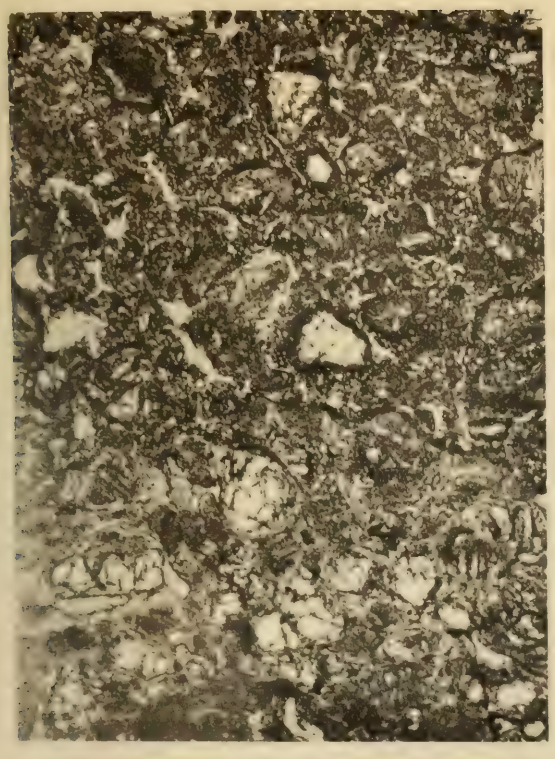
Fig. 4.—Sheffield silica-brick. E. 11465. × 32 diams.

EXPLANATION OF PLATE V.

Used silica-brick from the roof of an acid open-hearth steel furnace, showing zones of alteration. Dimensions after use:—

Length, $6\frac{1}{4}$ inches. Width, $3\frac{1}{8}$ inches.

A detailed description is given on page 65.



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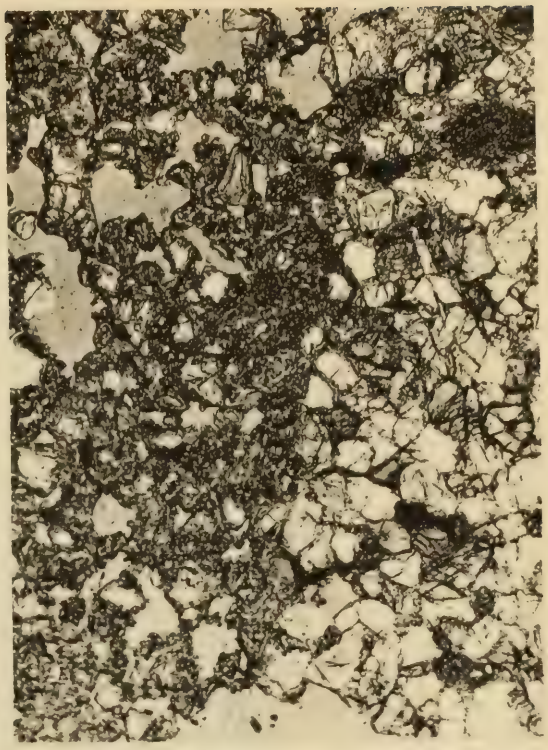

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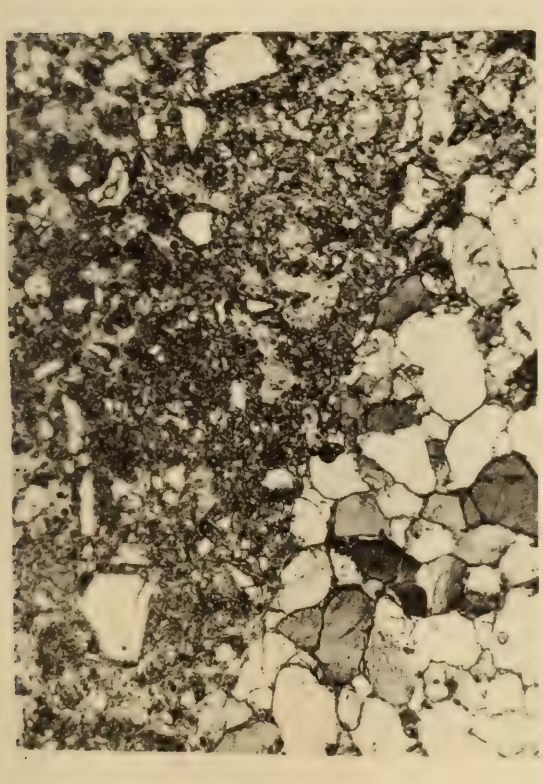

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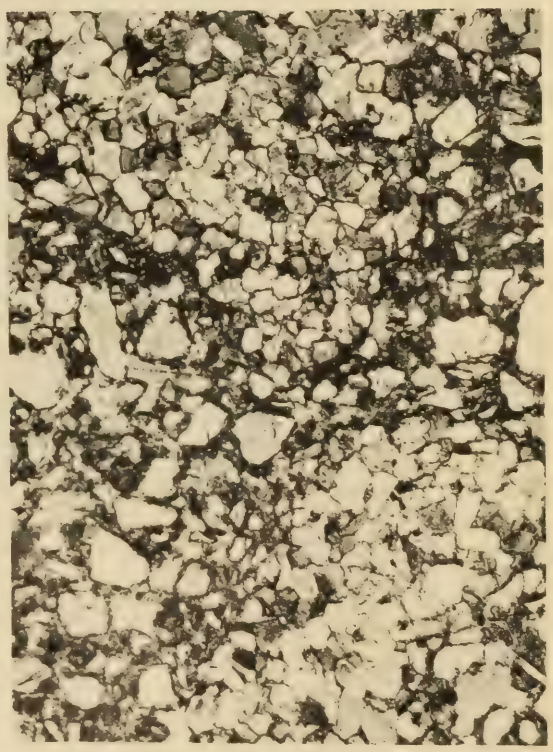

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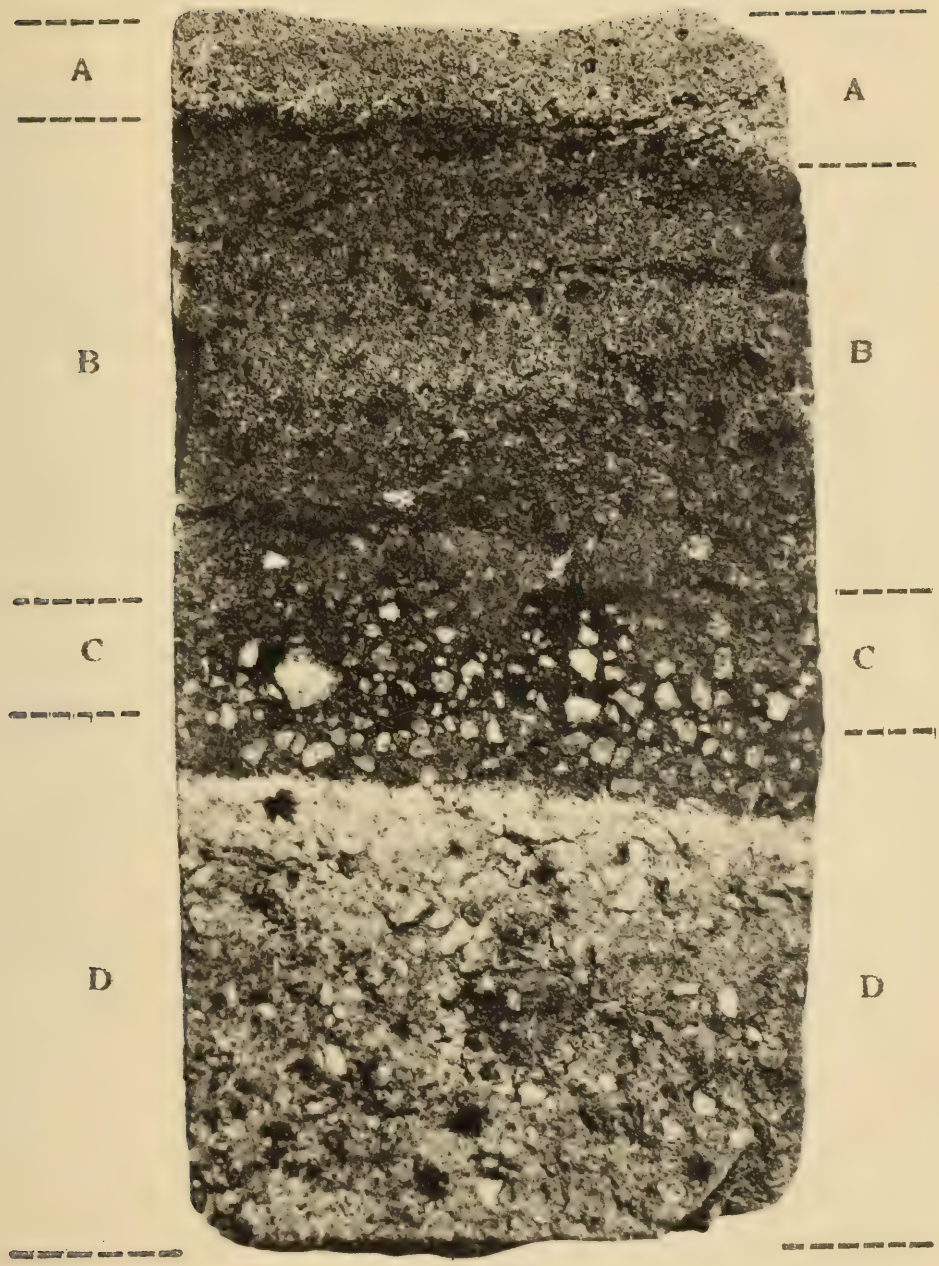
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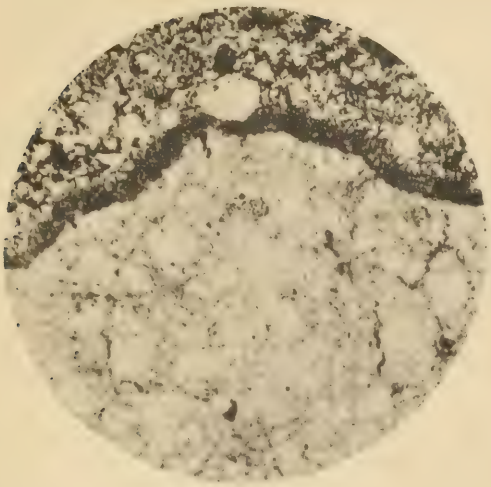

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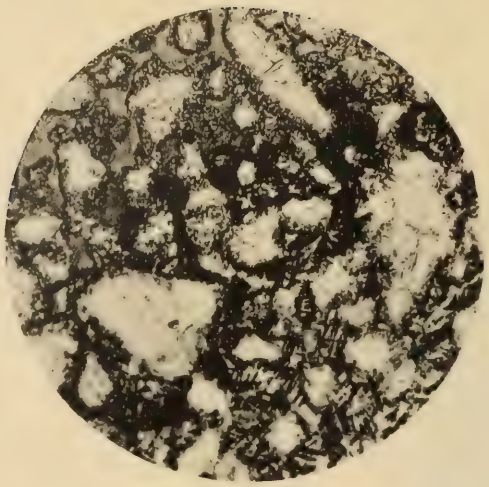

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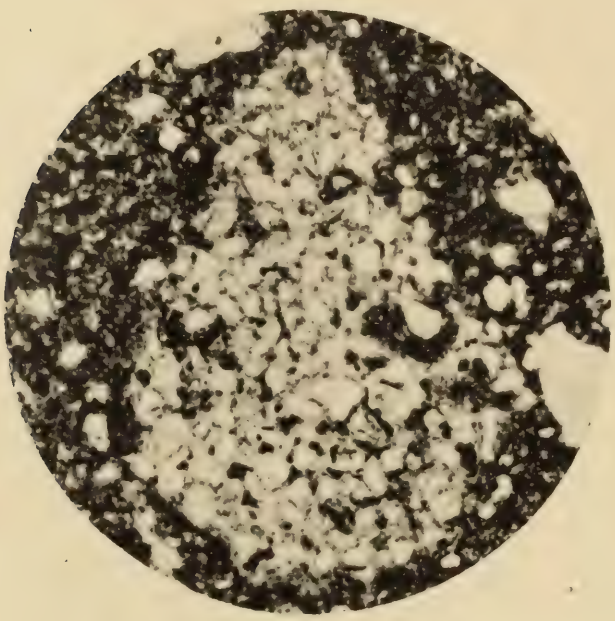

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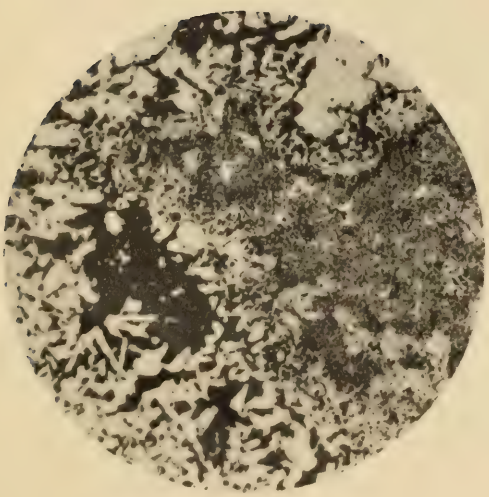

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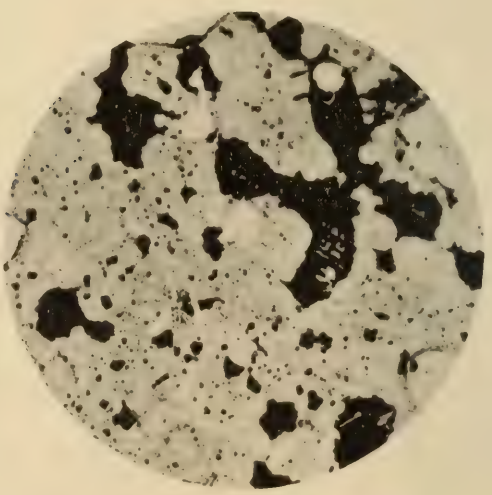

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EXPLANATION OF PLATE VI.

MICROSECTIONS OF THE USED ROOF-BRICK.

FIG. 1.—Partly altered ganister fragment in a ground-mass of magnetite and tridymite. Zone C. × 30 diams.

FIG. 2.—Limit of penetration of magnetite. Grains of unaltered ganister surrounded by fringes of tridymite in a glassy matrix that contains dendritic crystals of magnetite on the side that has been nearer the furnace. Junction of Zones C and D. × 24 diams.

FIG. 3.—Ganister fragment showing partial conversion and penetration by magnetite. Zone B. × 30 diams.

FIG. 4.—Ganister fragment completely converted to tridymite, and penetrated by finely-divided magnetite in a coarse ground-mass of tridymite and magnetite. Zone B. × 24 diams.

FIG. 5.—Aggregate of granular cristobalite with interstitial slag that consists of magnetite with a little silica. Zone A. × 24 diams.

EXPLANATION OF PLATE VII.

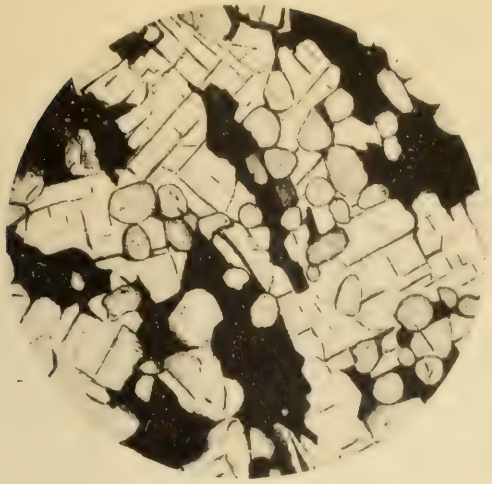
FIG. 1.—Bank of basic furnace, about three inches below the surface. Granular yellow periclase, crystalline lime showing well-defined cubic cleavage, and a silicate deeply stained with iron. From a drawing. × 100 diams.

FIG. 2.—Bank of basic furnace. A fine grained aggregate of granular periclase, lime and lime silicates. × 20 diams.

FIG. 3.—Quartz sand penetrated by ferruginous slag, heated for one-and-a-half hours at 1,400° C. The quartz grains are bordered by fringes of tridymite. E. 11536. × 30 diams.

FIG. 4.—Used roof-brick. Coarse aggregate of tridymite and magnetite. Zone B. × 30 diams. E. 11702. Ordinary light.

FIG. 5.—Used roof-brick. Aggregate of tridymite and magnetite. Zone B. Many of the crystals of tridymite show the characteristic arrow-head twinning. E. 11702. × 55 diams. Crossed nicols.



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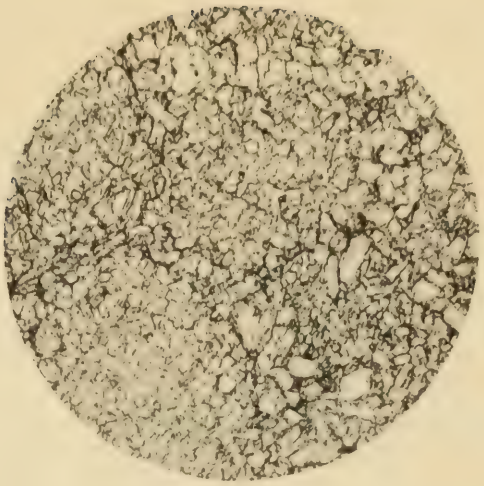

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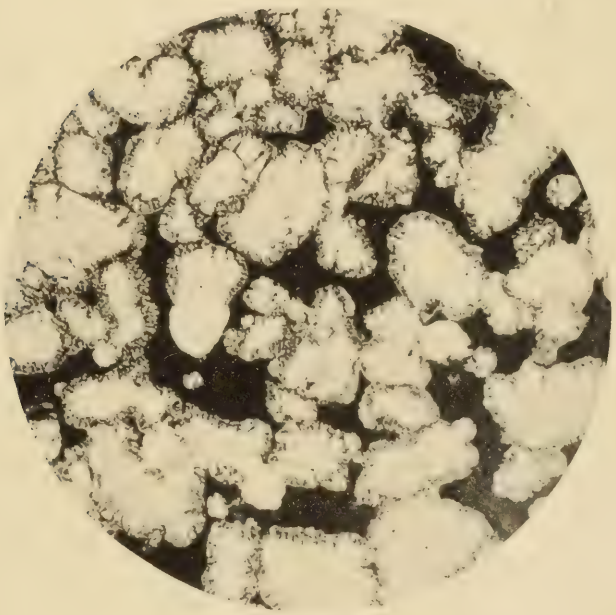

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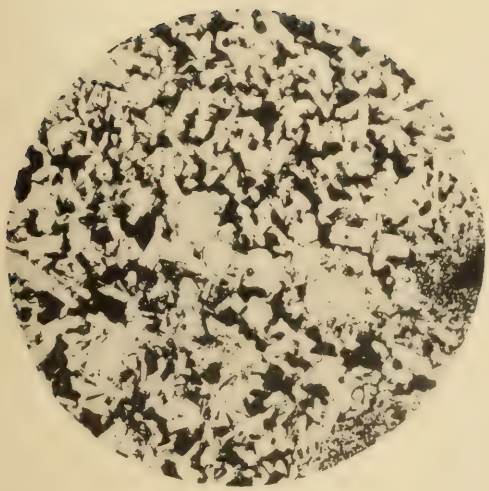

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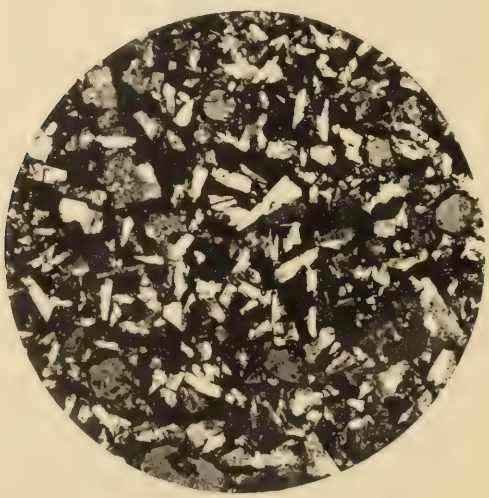

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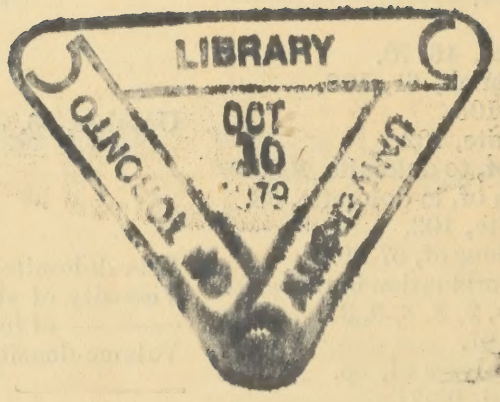
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